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JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Absorption-spectra of the Rare Earths. By G. H. BAILEY (*Ber.*, **20**, 2769—2770).—Krüss and Nilson have recently published (Abstr., 1887, 890) the results of experiments on the absorption-spectra of solutions of certain minerals containing the rare earths; a comparison of various intensities of the absorption-bands observed, induces them to believe in the existence of some 20 new elements. It is here pointed out, firstly, that it is exceedingly difficult to judge the relative intensities of absorption-spectra; and, secondly, that it is impossible to compare, for example, solutions which contain little or no erbium or samarium with those which contain salts of these metals in greater quantity. Thirdly, no consideration is given to the influence of the solvent on the intensity of the absorption-band. On these grounds, the author considers that the evidence brought forward is insufficient to prove the existence of these new elements.

V. H. V.

Action of Light and Reducing Agents on Silver Salts: Formation of Photo-salts. By M. C. LEA (*Amer. J. Sci.*, **33**, 349—364, 480—488, 489—494; and **34**, 33—36).—It is possible to obtain compounds of silver with chlorine, bromine, and iodine which show varied and beautiful colours, are highly stable except when exposed to light, and can be formed by chemical methods in entire absence of light. These compounds are identical with the substances forming the invisible or latent photographic image, and many of them show a tendency to reproduce colours. The author proposes to call these compounds *photo-salts*, a name which recalls one of their modes of origin without involving any statement as to their chemical nature. They are formed from the normal salts by the action of reducing agents, and contain a lower proportion of the halogen than the normal salts, but their high stability indicates that they are not sub-salts, and do not contain any free sub-salt. It is most probable that they are compounds of the sub-salts with large proportions of the normal salts, and are analogous in constitution to the "lakes" formed by colouring matters. Their composition varies considerably according to the method of preparation.

Silver Photochloride.—Compounds of silver with chlorine can be obtained with various shades of colour, ranging from white through flesh-colour, pale-pink, rose, copper-red, reddish-purple, and chocolate, to black.

Finely divided metallic silver, obtained by reduction in the wet way, treated for several hours with successive portions of a strong solution of sodium hypochlorite, yields a product which is purple-black, and sometimes even black. If the action is complete, nitric acid of sp. gr. 1·36 removes no silver, the substance, therefore, contains no metallic silver and no subchloride, as the latter would be at once decomposed. Subchloride is at first formed, but is converted into the normal chloride, which at once combines with other subchloride, forming a photo-salt, and thus removing the subchloride from the sphere of action. This process continues until the whole of the silver is converted into a compound of silver subchloride with the normal chloride. Prolonged action of the hypochlorite beyond this point gradually reduces the amount of sub-salt present.

Strong nitric acid destroys all varieties of the photochloride, but the degree of resistance to its action varies widely, and is sometimes very considerable, a fact which is the more remarkable since freshly precipitated subchloride is at once decomposed even by dilute nitric acid.

When protected from light, the photochloride prepared by the above method remains unaltered, even after 18 months. It is far more slowly attacked by ammonia than the normal chloride, several hours being required for complete solution even with a large excess of ammonia. Eventually only metallic silver soluble in nitric acid remains. If the ammonia is poured off shortly before this point is reached, and the undissolved portion is treated with nitric acid, a black residue is left, consisting of metallic silver mixed with a very dark variety of the chloride. This dark variety is insoluble in any acid, and has been mistaken for a passive modification of metallic silver. Some preparations of this dark chloride contained 2·49 per cent. of subchloride, and 97·51 per cent. of the normal chloride.

If a solution of normal silver chloride in ammonia is added to a solution of ferrous sulphate, allowed to remain for one minute, and then mixed with dilute sulphuric acid until strongly acid, the product well washed, boiled with dilute nitric acid, again washed, treated with hydrochloric acid, and finally washed, a brilliant red photochloride is obtained, its colour resembling that of electrolytic copper. The beauty of the preparation depends on the complete removal of metallic silver and of iron compounds. Any silver salt, for instance, the phosphate, will give a similar result.

Silver oxide is heated for a long time at 100°, or is roasted until the colour changes from brown to black, care being taken to avoid absorption of carbonic anhydride, and it is then treated with hydrochloric acid; or silver carbonate is roasted until black, and then treated with hydrochloric acid. The product has a pale-pink, copper-red, deep red, or burnt carmine colour, according to circumstances.

Ferrous sulphate mixed with excess of potassium hydroxide, then with a solution of a silver salt, and finally with hydrochloric acid, yields a photochloride, the colour of which depends mainly on the amount of reduction. Manganous oxide behaves similarly, but the reducing action is weaker, and must be assisted by heat. Chromous oxide has still less effect, and with cobaltous oxide, reduction is scarcely perceptible without long-continued heating.

Ferric chloride behaves with metallic silver in much the same way as an alkaline hypochlorite, but is less energetic, one or two days being required for a complete reaction. If the action has taken place in the cold, the product is dark purple-black, and contains from 1·52 to 7·5 per cent. of silver subchloride. Prolonged contact with ferric chloride eventually converts the photo-salt into the normal chloride, especially on heating.

When freshly precipitated and moist silver subchloride is treated with nitric acid, there is a brisk effervescence with evolution of nitrogen oxides, but when the substance has been converted into a photochloride by the combination of the normal chloride with the unaltered subchloride, the action ceases. The proportion of subchloride varies from 1·96 to 8·62 per cent., and depends mainly on the strength of the acid and the duration of its action. The colour varies from rose to purple, and is always rendered paler by the removal of silver subchloride by prolonged action of nitric acid, although it by no means follows that the darkest varieties contain the highest proportion of subchloride. With sodium hypochlorite, silver subchloride yields a purple photochloride.

Cupric chloride attacks silver in the same way as ferric chloride, and the action is more energetic, but the removal of copper from the product is difficult. In one case the proportion of subchloride in the photo-salts was 6·28 per cent. If a very dilute solution of silver nitrate is added to cuprous chloride, and the bulky, black powder which is formed is boiled with nitric acid, a red photochloride is obtained.

When a solution of silver chloride in ammonia is added to ferrous chloride, and the greyish or olive-black precipitate is washed with dilute sulphuric acid, it becomes brownish-purple, and the colour is still brighter after treatment with nitric acid. One specimen contained 4·26 per cent. of subchloride.

If hydrogen is passed over silver citrate at 100°, and the product is treated with hydrochloric acid and then with nitric acid, it yields a fine purple photochloride, which in one case contained 3·11 per cent. of subchloride.

A very good method is to act on a silver salt with potassium hydroxide and an organic substance such as lactose, dextrose, gum, tannin, alcohol, &c. The time required varies widely, a few minutes being sufficient with lactose, whilst dextrin requires half an hour. The product is mixed with hydrochloric acid, and after washing is boiled with nitric acid. The best result is obtained if the product is chestnut-brown after adding hydrochloric acid. At this stage, it contains 92·68 per cent. of silver, and is a mixture of normal chloride, subchloride, and metallic silver. After boiling with nitric acid, it is purple or burnt carmine. One sample obtained with dextrin contained 2·26 per cent. of subchloride; another prepared with lactose contained only 0·34 per cent.

If ferrous sulphate solution is mixed with hydrochloric acid and silver nitrate added, the precipitate is white, but if the silver nitrate is mixed with ammonia in quantity insufficient to neutralise the acid in the iron solution, a photochloride is precipitated which is at first dull purple, but is improved by treatment with hydrochloric and nitric acid.

Potassium ferrous oxalate with silver nitrate yields a black powder which is converted into a deep purple photochloride by treatment first with hydrochloric and then with nitric acid. Ammoniacal silver nitrate with aqueous pyrogallol containing excess of hydrochloric acid gives a grey precipitate, which when washed and treated with hot dilute nitric acid, yields a bright pink photochloride. Silver nitrate mixed with ferrous sulphate yields metallic silver, but if soda or potash is first added, and afterwards hydrochloric acid, red photochloride is obtained. Silver nitrate mixed with excess of sodium carbonate, then added to ferrous sulphate solution, and afterwards treated with hydrochloric acid, yields a photochloride. Photochlorides are also formed when freshly precipitated silver chloride is boiled with finely divided silver and then treated with nitric acid; when the fused normal chloride is partially reduced with zinc and sulphuric acid and treated with nitric acid; when silver is treated with hydrochloric acid mixed with potassium dichromate or permanganate; and when silver is mixed with potassium chloride and chlorate and dilute nitric acid cautiously added.

Photochlorides become purple and purplish-black when exposed to light. With mercuric chloride, they become dirty white; with mercuric nitrate, they dissolve and seem to be decomposed, since they can only be recovered as white normal chloride. Potassium chloride has no effect; with potassium bromide, they become dull lilac; with a small quantity of potassium iodide, they are instantly changed to bluish-grey; with a large quantity, they dissolve somewhat readily, and in time solution is almost complete. Potassium chlorate and hydrochloric acid convert the photochlorides into normal chloride. They show a decided tendency to become red when heated. The change in colour produced by boiling with nitric acid is due to the action of heat, the removal of metallic silver, and the decomposition of uncombined subchloride. It is not possible to dissolve out the normal chloride by means of an alkaline chloride; when boiled with ammonium or sodium chloride, the photochlorides gradually dissolve, a residue of metallic silver being left.

Silver chloride precipitated with excess of hydrochloric acid and exposed to light until it becomes very dark, and then treated with nitric acid of sp. gr. 1·36, yields only a trace of metallic silver. A small quantity of subchloride is formed by the action of light, and combines with the unaltered normal chloride. A small quantity of metallic silver or of uncombined subchloride is formed at the same time. When a small quantity of the subchloride has been produced, and has formed a photochloride, decomposition ceases.

The brighter coloured varieties of the photochlorides cannot be obtained by the action of light on the normal chloride, but when many silver salts, such as the oxalate, phosphate, tungstate, carbonate, pyrophosphate, and acetate are exposed to light and then treated with hydrochloric acid and with nitric acid, pink, red, and purple products are obtained, which agree in properties with the products of reduction. The photochlorides obtained by different methods are not identical, and vary considerably in their resistance to the action of light, ammonia, and nitric acid. As a rule, the darker varieties are the most stable.

When the rose-coloured photochloride is exposed to the spectrum, it becomes violet in the violet, slate-blue in the blue, is bleached in the green and yellow, and remains unchanged in the red. The maximum effect is near F, and there is a second feebler maximum at the end of the visible violet. With coloured glass, the results are more marked. Under two thicknesses of ruby glass, the colour becomes brighter and redder; under blue, sometimes blue, sometimes grey; under cobalt glass, deep blue; under manganese glass, violet; green and yellow have little effect. The dark varieties of the photochloride do not give such good results as the rose and copper shades. The latter closely resemble the films prepared by Becquerel both in their behaviour to light and when heated, and they are probably identical in composition. The action of light on photochlorides is affected by the presence of other substances, especially such as can give up chlorine. The red chloride darkens in white light, but if mixed with lead chloride, zinc chloride, and certain other chlorides, it bleaches to a considerable extent.

Photobromides are obtained by the same reactions as the chlorides, but the coloured products are not always true photo-salts. Silver bromide with reducing agents sometimes gives a brown form of metallic silver, which when mixed with unaltered bromide resembles a photo-salt in appearance but not in properties. Cold nitric acid dissolves silver from this mixture, but has no action on a photo-salt.

A very fine purple variety is obtained by the action of ferrous hydroxide, but its composition is very variable. One sample contained 7·25 per cent. of subbromide. Six grams of silver nitrate is dissolved in 200 c.c. of water, and ammonia added until the precipitate redissolves; 12 grams of ferrous sulphate is dissolved in 200 c.c. of water, and then mixed with the silver solution and with a solution of 4 grams of sodium hydroxide in 50 c.c. of water. After standing for a few minutes, 5 grams of potassium bromide in a little water is added, and dilute sulphuric acid until strongly acid. The product is washed, and heated cautiously with nitric acid of sp. gr. 1·36 diluted with 5 vols. of water. The photobromide thus obtained has a very fine purple colour, and contains somewhat less than 1 per cent. of subbromide.

Other suitable methods for preparing photobromides are to add an ammoniacal solution of a silver salt to ferrous sulphate and then treat with hydrobromic acid, or to act on a silver salt with potassium hydroxide and an organic substance and then add hydrobromic acid.

A dilute solution of potassium iodide reduces the colour of the photobromides; a strong solution dissolves them, and yellow normal bromide is precipitated on dilution. Acid ferric sulphate has no action in the cold, but the normal bromide is formed on heating. Ammonia acts more slowly than on the photochlorides. Sodium thiosulphate dissolves the photobromides, leaving a residue of metallic silver. When exposed to light, they darken very much more rapidly than the photochlorides, and the images readily undergo reversal when treated with an ordinary developer. They are much more sensitive than the normal bromide. In the spectrum, the photobromides show little tendency to reproduce colours. Under coloured glass, the results are more marked, but are inferior to those obtained with the photochlorides; they become greenish under blue glass, blue under green, are bleached under yellow, and unchanged under red.

Photoiodides are obtained by methods similar to those employed for the preparation of the photobromides and photochlorides, but are readily decomposed by a slight excess of the alkaline salt. A bright purple variety is obtained by adding iodine to a solution of potassium hydroxide until almost black, diluting with water, and adding gradually to finely divided, reduced silver. The product is then boiled cautiously for a very short time with nitric acid of sp. gr. 1·36 diluted with 12 to 15 vols. of water. Great care is required to avoid conversion of the photoiodide into the normal iodide. Another method is to mix silver nitrate solution with a considerable excess of ammonia, pour the mixture into ferrous sulphate solution, and then add potassium iodide dissolved in dilute sulphuric acid, care being taken to avoid excess of iodide. Excess of silver is removed by means of nitric acid. The proportion of subiodide in the photoiodide varies from 0·64 to 4·63 per cent. The photoiodide cannot be obtained by the action of hydriodic acid on roasted silver oxide.

When normal silver iodide is treated with sodium hypophosphite solution, a brown product is obtained, but the liquid takes up no iodine. It is found, however, that silver iodide can absorb and retain small quantities of free iodine; precipitated silver iodide will in fact decolorise a dilute solution of iodine. This fact explains the gradual disappearance of the invisible or latent images on silver iodide films formed by treating silver with iodising solutions. The silver iodide formed absorbs small quantities of free iodine. When the film is exposed to light, subiodide is formed, and combines with the normal iodide, forming photoiodide, but the free iodine in the film gradually reconverts the photoiodide into normal iodide, and the image is destroyed. This disposes of the last argument in favour of the physical theory as to the nature of the invisible image.

With ammonia, the photoiodides become salmon-coloured, but undergo no further change; there is no separation of metallic silver. Sodium thiosulphate dissolves the photoiodides, leaving a slight residue. Dilute nitric acid mixed with dilute potassium iodide solution converts them into normal iodide. When exposed to light, the photoiodides become greenish-grey, and the image obtained by development is usually direct, but is occasionally reversed, the photoiodide being intermediate in this respect between the photochloride and photobromide.

Identity of Photo-salts with the Substances forming the Invisible Image.—Sodium hypophosphite has no visible action on silver chloride, bromide, or iodide in the cold, but produces an invisible effect, and renders them sensitive to the action of a developer. If the solution is concentrated, and is heated, brownish-purple protochloride, bromide, or iodide is obtained. Well washed precipitated silver chloride is mixed with a strong solution of sodium hypophosphite and heated for 10 to 15 minutes, then washed and treated with very dilute nitric acid. A pink or reddish-brown product is obtained, which contains 1·77 to 3·53 per cent. of subchloride, and is much more readily attacked by nitric acid than the other varieties of photochloride. By prolonged action of the hypophosphite, silver chloride is reduced to metallic silver.

In the entire absence of light, sodium hypophosphite is able to produce in a sensitive film of a haloïd salt of silver a change exactly similar to that produced by light, that is, an invisible image capable of development, and just as light always produces a direct image on silver chloride, but under certain conditions a reversed image on silver bromide, so the hypophosphite always produces a direct image on the chloride, but sometimes a reversed image on the bromide. In both cases, too, prolonged action produces a visible image.

Experiments in this direction are readily made by steeping paper in a solution of soluble chloride or bromide, drying, and then floating on a solution of silver nitrate, washing, and drying. Lines, &c., drawn on such paper with sodium hypophosphite solution are invisible, but can be developed by potassium ferrous oxalate solution or any ordinary developer. The action increases with the time and also with a rise of temperature.

A similar result is obtained with a very dilute solution of potassium hydroxide mixed with lactose or other easily oxidisable organic substance. Both cases are the initial stages of reactions which when prolonged give rise, like the action of light, to the formation of photo-salts.

Chloride, bromide, and iodide paper were exposed to light and then cut in half, one half of each being immersed for five minutes in strong nitric acid, and then washed thoroughly and placed in the same developing solution. The image on the chloride is almost unaffected, that on the bromide has become weaker but is still strong, whilst that on the iodide is completely destroyed. Pieces of the same paper were treated with sodium hypophosphite solution, and one half of each piece immersed in nitric acid. On development, the results were precisely the same as with the images produced by light. The invisible image produced by light is not very materially affected by cold concentrated solutions of potassium chloride or bromide, but is destroyed by a solution of potassium iodide; the invisible image produced by the hypophosphite behaves in exactly the same way.

The action of light on silver chloride always results in a direct image on development, but with the bromide the image gradually becomes weaker as the action of light is prolonged, and eventually the image is reversed, that is to say, the exposed portions of the sensitive film offer greater resistance to the action of the developer than the unexposed portions. Bromide-paper treated with a 20 to 30 per cent. solution of sodium hypophosphite gives a direct image on development, but if a more and more dilute solution is employed, the image becomes weaker and weaker, at last reaching a point at which there is no apparent effect, but with still greater dilutions development gives white marks on a dark ground. The effect is similar to that produced by light, but is in the inverse order.

Sodium hypophosphite reverses the action of light and *vice versâ*. If lines are drawn with a concentrated solution of the hypochlorite upon bromide-paper which has been exposed to light, and the paper is then treated with a developer, the lines appear white on a dark ground. If the red or purple photobromide obtained by the action of the hypophosphite or other reducing agent is applied to paper in the form of a film, and exposed to light, and then treated with potassium ferrous oxalate, the exposed portions appear as white upon a dark ground, although before development they were darker than the photobromide. It follows that the photobromide, like the ordinary bromide, is capable of reversal.

When a film of silver tartrate, citrate, benzoate, pyrophosphate, or other stable salt is formed on paper in the usual way, exposed to light under a negative, treated with hydrochloric or hydrobromic acid for some time, well washed, and developed with potassium ferrous oxalate, an image is formed similar to that which would be obtained on a film of chloride or bromide. It follows that one silver salt may be converted into another without losing its property of being reduced when treated with a developer, and it is evident that all such salts must be capable of forming sub-salts. The general existence of such sub-salts has not hitherto been suspected.

After such an image has been treated with hydrochloric or hydrobromic acid, it may be treated with nitric acid until all silver compounds, except the haloïd salt, are removed from the paper, but on development the image is brighter and stronger. It follows that the product of the action of hydrochloric or hydrobromic acid on the exposed silver tartrate, citrate, &c., is identical with the product of the direct action of light on silver bromide or chloride. If paper prepared with silver tartrate, oxalate, &c., is exposed to light, part of it treated in the dark with hydrochloric or hydrobromic acid, washed with nitric acid, and afterwards developed, the portions treated with the haloïd acids give a black image, whilst the other portions remain white, a fact which shows that the sub-salts of the tartrate, oxalate, &c., are soluble in nitric acid. When the tartrate or oxalate paper is exposed to light for a short time, marked with hydrochloric or hydrobromic acid and treated with a developer, the marks develop first, and hence the subchloride or subbromide is more susceptible to the action of the developer than the subtartrate or suboxalate. The greater sensitiveness of the haloïd salts may be due to their power of combining with their own sub-salts, so that the reduction which begins with the sub-salt quickly extends to the normal salt with which it is combined. Other silver salts have not this power, and therefore are more slowly and irregularly attacked by developing solutions.

When paper prepared with silver tartrate, oxalate, &c., is exposed to light, treated with hydrochloric acid and developed, the effect of a short exposure is the same as that of a long exposure. A short exposure produces sufficient alteration to serve as a nucleus for development; a long exposure does no more. C. H. B.

Spectrum Researches on the Energy of the Action of Bromine on Aromatic Hydrocarbons. By J. SCHRAMM and I. ZAKRZEWSKI (*Monatsh.*, 8, 299—309).—Sunlight was reflected through a vertical slit by a heliostat on to a condensing lens of great focal length. By means of a bisulphide of carbon prism, a spectrum 80 cm. long was produced, in which Fraunhofer's lines were distinctly visible. Nine test-tubes were fastened at equal distances between the lines B and H, since preliminary experiments showed that the chemical action was confined to the space between these lines. A few drops of bromine were added to the solution of the carbon-compound, and the mixture was equally distributed among the test-tubes. The time occupied from first illumination to total disappearance of the bromine was observed in each tube. To exhibit graphically the energy of the reaction, curves are plotted, so that the abscissæ indicate the part of the spectrum and the ordinates the reciprocals of the duration of the reaction. In this way experiments were made on toluene, ethylbenzene, and metaxylene. All the researches showed that the maximum action takes place in the yellow or yellow-green. The blue and violet rays exert a slight action, and the dark-red scarcely any at all. The curves are therefore similar in character to that for the intensity of light in the spectrum. C. S.

Increase of Photo-electric Currents. By J. MOSER (*Monatsh.*, 8, 373).—The author finds that the electromotive force produced by the action of sunlight on chloride, iodide, or bromide of silver plates can be considerably increased by immersing them in a bath of a dye, say, erythrosin. C. S.

Electric Properties of Rock-salt. By F. BRAUN (*Ann. Phys. Chem.* [2], 31, 855—872).—Although this substance is isotropic as regards light, its modulus of elasticity according to Voigt is 4170, 3400, and 3180 kilo. per sq. cm. in directions parallel respectively to normals to the cubical, dodecahedral, and octahedral faces. On Maxwell's theory, high insulating properties might be expected in it, since it is highly diathermanous. It is in fact so good an insulator, although not perfect, that its dielectric constants could be well determined.

Much of the paper is devoted to describing the methods of determining the constants of the instruments used. The ends of a rock-salt column were cut parallel to cubical faces, a hole drilled length-wise nearly through its axis, and the vertical edges planed away until the section of the column was octahedral. Alternate faces were then cubical and dodecahedral. Plates of tinfoil were attached to two of these, and, the inner chamber being filled with mercury charged to a high potential, the charges on these were compared by the electrometer. Within the limits of experimental error, the charges were found to be equal. Similar experimens with two little condensers constructed from plates parallel to cubical and octahedral faces showed the dielectric constants of these also to be the same. Absolute measurements were not made.

The conductivity was also measured by the electrometer. One plate of a little rock-salt condenser was joined to a battery of 16 large Leyden jars, the potential of which (1500 to 3000 volts) was observed from time to time, so as to calculate the rate at which its charge was dissipated through leakage. The other plate being joined to the electrometer, the indications of the latter afforded a measure of the conductivity. The method is fully described: the results are as follows (specific resistance of mercury = 1).

Specific resistance perpendicular to cubical face $= 1{\cdot}33 \times 10^{21}$.
" " " octahedral face $= 2{\cdot}63 \times 10^{21}$.

Ratio of resistance perpendicular to cubical face to resistance perpendicular to dodecahedral face = 3 : 2.

Specific resistance of paraffin $= 3{\cdot}02 \times 10^{22}$.

The dielectric constants were also found to be independent of the time of electrification.

The provisional conclusion is, that rock-salt is dielectrically isotropic, but anisotropic as regards conductivity. Ch. B.

Validity of Joule's Law for Electrolytes. By H. Jahn (*Ann. Chem. Phys.* [2], **31**, 925—940; see also *ibid.*, **25**, 49).—The object of these experiments was to ascertain whether the portion of the current energy expended on polarisation during electrolysis contributes to the development of heat or not. The method of inquiry consisted in measuring the heat developed during the electrolysis of antimony chloride between antimony electrodes, in a cell enclosed in a Bunsen's ice-calorimeter, and the current flowing through the circuit, and calculating Joule's constant a from the equation—

$$W_{s.c} = aJ(iR - J\rho),$$

where W = heat developed per second in the calorimeter, iR = difference of potential between two points in the circuit including the cells, ρ = resistance of the part of the intervening circuit not included in the cell, and J = strength of current. Antimony chloride was selected on account of the high polarisation generated during its electrolysis.

Since antimony separates from its chloride sometimes in the ordinary form, sometimes in the explosive form, experiments were made with electrodes of both kinds. During the rapid rise of the polarisation (about five minutes) the strength of the current E was assumed to vary according to the law $E = E_0 + at + bt^2$. The total current was then determined by summation from observations at intervals of five minutes. From various experiments it was found,

$$a = 0{\cdot}2367;\ 0{\cdot}2362;\ 0{\cdot}2375;\ 0{\cdot}2376;\ 0{\cdot}2383;\ 0{\cdot}2382.$$

The author shows that if the polarisation energy did not contribute to heat development the result should have been $a = 0{\cdot}2693$.

Ch. B.

Conductivity of Pure Water, and its Temperature Coefficients. By E. Pfeiffer (*Ann. Phys. Chem.* [2], **31**, 831—855).—This paper refers chiefly to the conductivity of water contained in glass vessels, and hence rendered more or less impure by dissolution of the glass substance. Kohlrausch's method was used. One of the electrolytic cells has been already described (*ibid.*, **25**, 232). A second form consisted of two platinum plates (3 cm. square) held at a fixed distance apart by glass rods fused to their faces, and suspended by the conducting wires in a glass vessel. Since the conductivity changes rapidly from the moment of filling, observations were made at regular intervals, and the initial conductivity calculated by extrapolation.

The solvent action on glass is always apparent, but increases greatly with the temperature. When successive charges of water are poured into a new glass vessel, the resulting time-rate of increase of conductivity is at first rapid, but after a time reaches a nearly constant minimum value which does not change for months. When the same mass of water is allowed to remain in a glass vessel at constant temperature for a long time, the time-rate of increase of conductivity grows gradually greater; from this the author concludes that the conductivity is not proportional to the amount of dissolved glass substance. He thinks that the suitability of different kinds of glass for chemical purposes might be usefully tested in this way.

The rapid fall in conductivity which takes place immediately after filling (Kohlrausch, *Ann. Phys. Chem* [5], **26**, 220; Pfeiffer, Abstr., 1886, 115) is attributable to the diffusion into the fresh liquid of a layer of the previous charge adhering to the glass and electrodes.

Temperature coefficients have been investigated by Kohlrausch, Vicentini, and Arrhenius. For different solutions, these tend towards equality with increasing dilution; for a particular electrolyte, the coefficient is nearly constant for highly dilute solutions of different strengths; for an excessively dilute solution, it at first decreases as the strength increases. Owing to the constantly changing strength of the solution, its determination for the particular electrolyte furnished by the soluble part of the containing glass vessel was laborious. The results are given in lengthy tables. The initial conductivity of the purest water used was $\lambda = 0{\cdot}65$ ($\lambda = k_{18} \times 10^{10}$) at 14°; and observations were continued until λ about equalled 20. Curves were then constructed showing the variations of the temperature coefficients $\alpha = \Delta_t/\lambda_{18}$. In one vessel, neglecting minor variations, as λ increased from unity α diminished to a minimum $0{\cdot}024$ at $\lambda = 3$, then increased to a maximum $0{\cdot}0269$ at $\lambda = 5$, and from $\lambda = 6$ onwards became constant at $0{\cdot}026$. In the second vessel (presumably of a different kind of glass), α reached a minimum for $\lambda = 2$, a maximum for $\lambda = 3{\cdot}5$, and became constant at $0{\cdot}023$ when $\lambda = 6$. For water which had previously remained for some time in a third vessel, the variations were similar, and α became constant when $\lambda = 9$. The initial variations amounted to about 12 per cent.

The law that the coefficient is constant for very dilute solutions appears to hold only so long as the electrolyte exceeds in amount the impurities (possibly organic) originally contained in the water.

Ch. B.

Formation of Hydrogen Peroxide at the Anode during the Electrolysis of dilute Sulphuric Acid. By F. Richarz (*Ann. Phys. Chem.* [2], **31**, 912—924; see also Abstr., 1885, 624, and McLeod, Trans., 1886, 591).—The author has repeated some of Berthelot's experiments (Abstr., 1878, 372; 1886, 607) on this subject, and in the main confirms his results. Sulphuric acid of 70 per cent. appears to be most suitable for developing hydrogen peroxide by electrolysis. In a 40 per cent. solution, persulphuric acid alone is formed. As a test for hydrogen peroxide in presence of persulphuric acid, the author recommends a solution of titanic acid in sulphuric acid. This gives an intensely yellow precipitate, which decolorises the same amount of permanganate as the peroxide which goes to form it. The peroxide may be estimated by permanganate in presence of persulphuric acid; and the latter subsequently estimated by adding ferrous sulphate in excess, and titrating back with permanganate.

Theories have been proposed by Hoppe-Seyler (*Zeit. physiol. Chem.*, **2**, 25) and Traube (Abstr., 1886, 660), who have shown that hydrogen peroxide can be formed at the cathode by reduction of molecular oxygen. The author accounts for its appearance at the anode. When a solution containing only sulphuric and persulphuric acids is allowed to remain, the latter gradually disappears, and hydrogen peroxide is at the same time formed. The author has studied this reaction quantitatively, but does not confirm Berthelot's statement that as decomposition goes on the ratio of hydrogen peroxide to persulphuric acid tends to become 2. In a dilute sulphuric acid solution, the decomposition is very slow, but it is greatly accelerated by adding strong sulphuric acid; from this the author concludes that the appearance of hydrogen peroxide at the anode in a strongly acid solution is always the result of this purely chemical reaction. Contact with a platinum plate almost entirely prevents the formation of hydrogen peroxide in a 40 per cent. sulphuric acid solution, although by catalysis it hastens the disappearance of persulphuric acid; especially when the platinum has been ignited, and consequently become charged with flame gases.

When a 68 per cent. acid solution is electrolysed by a current of 1·1 ampères, the quantity of hydrogen peroxide increases for about three hours, and then becomes stationary. The persulphuric acid, however, goes on increasing. On breaking the current, the peroxide at first noticeably increases, but the persulphuric acid rapidly disappears.

The fact that water is under certain circumstances oxidised by active oxygen, in conjunction with the fact that the peroxide is not directly formed at the anode during electrolysis, is a proof that the molecules of water cannot be electrolysed. The real anion is SO_4, and from this oxygen can only be liberated as O_2 or O_3. Traube supposes that peroxides which contain an even number of oxygen-atoms can alone form H_2O_2; and that those formed at the positive pole during electrolysis, and which contain an uneven number of such atoms, cannot form H_2O_2. The decomposition of persulphuric acid clearly contradicts this latter view. CH. B.

Electromotive Dilution Constants. By J. MIESLER (*Monatsh.* **8**, 365—372).—The electromotive force of polarisation alone was measured at the beginning and end of each experiment (to test its constancy) by means of a Siemens' universal galvanometer and a capillary electrometer. Next the concentration cell was introduced, so that the electromotive force due to difference of concentration aided or opposed the electromotive force of polarisation. By subtracting or adding the electromotive force of polarisation, the electromotive force due to differences of concentration was determined from the observed total electromotive force. Thus the following values of dilution constants in millivolts were obtained:—

	Acetate.	Sulphate.	Nitrate.	Chloride.	Bromide.	Iodide.
Cadmium .	1·5	2·8	—	—	—	—
Copper ...	2·3	3·6	—	—	—	—
Lead	2·6	—	8·3	—	—	—
Zinc.....	5·9	—	11·6	13·4	11·9	10·4
Silver.....	10·7	12·0	16·2	—	—	—

Taking any two rows in the table, it will be seen that the numbers in corresponding columns have a constant difference (Moser's law), whilst in the case of the three haloïd salts of zinc the differences of values of the dilution constants have an obvious relation to the atomic weights of the halogens. C. S.

Influence of Ultra-violet Light on the Electric Discharge. By H. HERTZ (*Ann. Phys. Chem.* [2], **31**, 983—1000).—The author has discovered that ultra-violet radiation favours the electric discharge between two conductors in a remarkable way. As sources of such radiation, the sun, burning magnesium, or even ordinary flame, may be used; but by far the most effective are the electric arc and an induced electric discharge. To produce the phenomenon, the primary circuits of two induction coils, a large one (10 cm.) and a smaller one (1 cm.), are joined in circuit with the same battery (six Bunsens) and interruptor. Perfect synchronism in the induced discharge is thus secured. The terminals of the large coil being arranged to give a good spark 1 cm. in length, the two coils are placed close together, and an opaque screen interposed. The terminals of the small coil are then drawn apart until sparks just cease to pass. On now removing the screen the discharge is re-established.

The author describes many experiments to test the nature of the effect. The influence is not electrical, since non-conducting screens are effective as well as metal plates. It varies in some inverse ratio with the distance, and is distinctly produced when the coils are 1 m. apart. In the above experiment, the larger spark may be either short and dense, or long and zig-zag, and every part of it is effective. The smaller spark, however, should be short (between knobs); the seat of the action upon it appears to be in the neighbourhood of the cathode or negative pole. The influence is reciprocal; that is, the smaller spark also favours the larger. The action is propagated in straight lines, like light, and may be reflected from polished surfaces. It may also undergo refraction; but its refrangibility (roughly measured by means of a quartz prism) is much greater than that of the violet rays. Most solid substances are opaque to it; amongst these glass, paper, agate, and mica, even in the thinnest sheets, are noticeable. Amongst crystalline substances, copper sulphate, topaz, and amethyst are opaque to it; but it is transmitted by sugar, alum, calc-spar, and rock-salt; transparent gypsum and rock crystal transmit it perfectly. Amongst liquids, water transmits it freely; sulphuric and hydrochloric acids, alcohol, and ether, less so; whilst melted paraffin and petroleum, benzene, bisulphide of carbon, ammonium hydrosulphide, and coloured liquids generally, stop it completely. Solutions of potassium, sodium, and magnesium sulphates, are fairly transparent to it; those of mercuric nitrate, sodium thiosulphate, potassium bromide and iodide, are very opaque. Amongst gases, air, hydrogen, and carbonic anhydride are very transparent; chlorine, and bromine and iodine vapours, partially so; and coal-gas and nitric peroxide very opaque.

Even an ordinary candle-flame may produce effects similar to those described, and may cause the reappearance of sparks between the terminals of an induction-coil after they have been drawn so far apart that the discharge has ceased. Similar effects are produced by the luminous flames of gas, wood, and benzene, and the non-luminous flames of alcohol, carbon bisulphide, and the Bunsen burner. Incandescent platinum, and the flames of sodium, potassium, sulphur, and phosphorus, and of pure hydrogen, are without effect. The effective rays are more refrangible even than the so-called photographic rays; for the latter are not sensibly absorbed by coal-gas.

CH. B.

Specific Heat of Liquid Carbon Compounds. By R. SCHIFF (*Gazzetta*, 17, 286—303).—In a former memoir (Abstr., 1887, 7), the author has shown that the variation of the specific heats in a homologous series of compounds is expressible either by a straight line, or a small number of parallel lines. In the equation for the mean specific heat $C_{t-t'} = a + b_{(t+t')}$, the coefficient b remains constant for all the terms of a homologous series, whilst the coefficient a either remains constant for all or several terms of the series, or varies *per saltum* with the molecular weight. These conclusions are confirmed in the present memoir, in which determinations are given of the specific heats of the ethereal salts of the chloro-substituted acetic acids and of the succinic acids, as also of certain aromatic compounds. The specific heats of ethereal salts of the propyl and allyl series are also compared. Thus it will be seen in the table below that the value for *b* in all the ethereal salts of mono-, di-, and tri-chloracetic acid is a constant = 0·00038, in those of the succinic acids = 0·00066, in aniline and toluidine = 0·0007. Further, the value for *a* in the allyl salts of propionic, butyric, and valeric acids is a constant = 0·433, but in other cases it varies somewhat indefinitely. From these results, the author concludes that neither isomerism nor change of molecular weight produces definite variations in the specific heats.

	a.	*b*.
Methyl chloracetate	0·3747	0·00038
Ethyl "	0·39	"
Propyl "	0·4067	"
Allyl "	0·3888	"
Methyl dichloracetate	0·3032	"
Ethyl "	0·3215	"
Propyl "	0·3335	"
Allyl "	0·3244	"
Methyl trichloracetate	0·2592	"
Ethyl "	0·2778	"
Propyl "	0·2892	"
Allyl "	0·2806	"
Allyl acetate	0·4305	0·00088
Isobutyl acetate	"	"
Allyl propionate	0·433	"
" butyrate	"	"
" valerate	"	"
" benzoate	0·3732	0·00075
Ethyl oxalate Propyl " Ethyl malonate Propyl "	0·4199	0·00066
Allyl oxalate	0·4122	"
Isobutyl oxalate	0·4274	"
Isoamyl "	0·4354	"
Ethyl succinate Propyl "	0·4391	"
Allyl "	0·4323	"
Isobutyl succinate	0·4421	"
Isoamyl "	0·4493	"
Aniline Orthotoluidine	0·4706	0·00070
Dimethylaniline	0·4018	0·00092
Diethylaniline	0·4343	"
Chlorobenzene	0·2988	0·00074
Chlorotoluene	0·316	"
Benzyl chloride	0·3225	"

V. H. V.

Heat of Formation of Zinc Ethyl. By GUNTZ (*Compt. rend.*, **105**, 673—674).—The zinc ethyl was decomposed by dilute sulphuric acid—

$ZnEt_2$ liq. + nH_2SO_4 diss. = $ZnSO_4$ diss. +
$2C_2H_6$ gas .... develops +79·8 Cal.

With hydrochloric acid, the number obtained is +78·0 Cal., but when these numbers are corrected for the heats of dissolution of the zinc salt in the excess of acid they become +80·8 and 77·8 respectively.

Taking the mean of these values, it follows that—

$ZnEt_2$ liq. + $2H_2O$ liq. = ZnH_2O_2 pptd. + $2C_6H_6$ gas .... develops +57·8 Cal.

the great development of heat explaining the rapidity with which this decomposition takes place. Further—

Zn solid + $2C_2H_6$ gas = $ZnEt_2$ liq. + H_2 gas absorbs −43·2 Cal.

and

Zn solid + C_4 solid + H_{10} gas = $ZnEt_2$ liquid absorbs −31·8 Cal.

The formation of zinc ethyl from its elements or from zinc and the hydrocarbon is accompanied by a very considerable absorption of heat. C. H. B.

Relation of Gases to the Laws of Marriotte and Gay-Lussac.

By C. PUSCHL (*Monatsh.*, 8, 327—337).—If $a = \frac{1}{v}\frac{dv}{dt}$ be the coefficient of expansion, and $c = -\frac{1}{v}\frac{dv}{dp}$ the compressibility, we have—

$$\frac{d(pv)}{dp} = v(1 - cp) = h \text{ say.}$$

When $h = 0$, Marriotte's law holds, and the gas will be more or less compressible than the law requires, as h is greater or less than 0.

For a gas at the critical temperature and compressed from an ordinary density, pv diminishes with the pressure, and h is therefore negative. As the pressure approaches the critical pressure, h diminishes and ultimately $= -\infty$. Further compression causes h to increase, and for a certain pressure $h = 0$. Here Marriotte's law holds. For greater pressures h is greater than zero, and the departure from Marriotte's law is in the reverse direction.

When the temperature of the gas is higher than the critical, h reaches a finite minimum during compression. This minimum increases with the temperature, and for a certain temperature the minimum value of h will be zero, and then both $h = 0$, $\frac{dh}{dp} = 0$. At still higher temperatures the minimum value of h will be positive, and pv will continually increase, as happens for example in the case of hydrogen. It appears therefore that the temperature for which $h = 0$, $\frac{dh}{dp} = 0$ simultaneously is the highest possible at which Marriotte's law can be exactly obeyed. The present method of consideration also shows that at a sufficiently low temperature hydrogen behaves like ordinary gases.

If we trace a curve with ordinate h and abscissa p, there will be a point on it for which h is a minimum. This point will lie above or below the axis of abscissæ, according as the temperature exceeds or falls short of that for which $h = 0, \frac{dh}{dp} = 0$. For the lower temperatures, the curve meets the axis in two points. At the point with the smaller abscissa, pv is a maximum for $\frac{d(pv)}{dp} = h = 0$, and also $\frac{dh}{dp}$ is negative. At the other point pv is similarly a minimum. Consequently for all gases a maximum value of pv will precede a minimum, and at a certain temperature above the critical temperature the two will coincide.

Again, when $h = 0$ and $\frac{dh}{dp} = 0$, we have—

$$\frac{dh}{dt} = pv\frac{da}{dp},$$

If, however, Marriotte's law be exactly obeyed—

$$\frac{dh}{dp}dp + \frac{dh}{dt}dt = 0,$$

and thus

$$\frac{dh}{dp}dp + pv\frac{da}{dp}dt = 0.$$

Since $\frac{dh}{dt}$ is positive, so also is $\frac{da}{dp}$, and for positive values of $\frac{dh}{dp}$, and for minimum values of pv, the pressure increases as the temperature diminishes. Since Amagat found in the case of oxygen the pressure at the minimum of pv decreases with rise of temperature, we infer this gas was nearly at that temperature where the maximum and minimum of pv coincide.

Similar reasoning is applied to the consideration of Gay-Lussac's law, and results of a very similar nature are deduced. C. S.

Highest Boiling Point of Fluids. By C. PUSCHL (*Monatsh.*, 8, 328—341).—A gas or fluid can be reduced to such a condition that v being its specific volume, p its pressure,

$$\frac{dp}{dv} = 0 \text{ and } \frac{d^2p}{dv^2} = 0,$$

or putting $e = -v\frac{dp}{dv}$,

$$e = 0 \text{ and } \frac{de}{dv} = 0.$$

Thus the zero value of e is a minimum for the critical state. If the temperature is lowered, the minimum value of e reached during compression is negative, and there must therefore be for every temperature two values of v, for which $e = 0$. At the greater value of v, $\frac{de}{dv}$ is positive, and p is a maximum, whilst the contrary holds for the less value. When the volume is greater than that for the maximum of p, the substance exists in the form of vapour, and when the volume is less than that for the minimum value, the substance is fluid. Between the two, the substance is in an unstable state.

A saturated vapour may be compressed, so that e changes from a positive value to zero, and then the tension is a maximum $= p'$. And in a similar manner, by sufficiently reducing the pressure on a fluid, the tension may be made a minimum $= p''$. For tensions $<p''$, the fluid will be in an unstable condition.

Suppose that a substance at a temperature above the critical fills a rigid vessel of such volume that the substance is of the critical density. If the temperature be lowered, $\frac{dp}{dt}$ will be positive. Thus whilst at the critical temperature the vapour-tension $p = p''$, at a lower temperature p is $< p''$. But in accordance with what precedes, the fluid and its vapour are now in unstable equilibrium. Also p'' at a sufficiently low temperature is negative. Thus there must exist a temperature somewhere below the critical when p again $= p''$. At this point, when the temperature is lowered, the substance suddenly appears liquid, and on the other hand with rise of temperature, it completely changes into vapour. This temperature is therefore defined to be the highest boiling point of the liquid. If the mass contained in the vessel be greater or less, the temperature of the highest boiling point will not be affected. C. S.

The Relation of Hydrogen to Marriotte's Law. By C. PUSCHL (*Monatsh.*, 8, 374—377).—As in his previous papers, the author traces the increase or decrease of the quantities, a, the coefficient of expansion, apv and h, by considering the signs of their differential coefficients. Since, according to Regnault's experiments, not only pv but also h increases as the pressure increases up to 20 m., he concludes that in order that h may have a minimum at greater compression, it must have first a maximum at a pressure above 20 mm. If hydrogen be allowed to expand, h will diminish, and we may conjecture that when the pressure is sufficiently small, h will be equal to zero. In this case, pv is a minimum. Since $\frac{dh}{dt}$ is positive, this minimum value will occur at greater pressures for diminishing temperature. In gases for which pv reaches a maximum through rarefaction, a minimum will occur on further rarefaction, and with diminishing temperature the maximum and minimum will approach towards coincidence. C. S.

Evaporation and Dissociation; Continuous Changes from the Gaseous to the Liquid State at all Temperatures. By W. RAMSAY and S. YOUNG (*Phil. Mag.* [5], 24, 196—212).—A further proof of the correctness of the formula $p = bT - a$ (where p is the pressure, b and a are constants for each separate volume of 1 gram, and T is the absolute temperature), is furnished by the behaviour of methyl and ethyl alcohols, under a very wide range of temperature, pressure, and volume. Tables are given showing the correspondence of numbers calculated by the above formula with those experimentally determined.

The expression bT is equivalent to the first term of Clausius's and Van der Waals' formulæ, $\frac{RT}{(v-\beta)}$, but it is by no means so simple. It would appear that b is not any simple function of the volume of the gaseous or liquid matter; and we are still in ignorance of the true relations between volume on the one hand, and pressure and temperature on the other. With constant volume, however, temperature and pressure have the simple relation already mentioned.

The behaviour of acetic acid was also investigated, and the data furnished by E. and L. Natanson (Abstr., 1886, 657) for nitric peroxide were also made use of. These two substances exhibit a behaviour markedly different from that of stable bodies. For whereas the isochoric lines (or lines of equi-volume) are straight with stable substances, when mapped against temperature and pressure as ordinates and abscissæ, those of acetic acid and nitric peroxide are curves of double flexure, tending at higher temperatures and pressures to become tangential to isochoric lines, calculated on the theoretical assumption that acetic acid and nitric peroxide have respectively the simpler formulæ $C_2H_4O_2$ and NO_2; and at lower temperatures and pressures approaching, as if they would ultimately touch, the theoretical isochoric lines of the more complex molecules $C_4H_8O_4$ and N_2O_4. The gradual dissociation of these molecules is thus traced, and these substances show and exhibit no analogy with stable substances. It cannot therefore now be asserted that the abnormal vapour-density of these compounds is ascribable to the same cause as the high vapour-density of stable substances at high temperatures and correspondingly high pressures.

The paper also shows the deviation from Boyle's and Gay-Lussac's laws exhibited by ether. It is to be noted that at any given volume smaller than 300 c.c. per gram, the pressure of vapour is below what is calculable on the assumption that ether gas is "perfect." At greater volumes, this divergence is barely noticeable by experiment. Keeping the volume constant, if the temperature and consequently the pressure be raised, there is a continually decreasing difference between the found and what may be called the "theoretical" pressure. At a certain sufficiently high temperature, the found and "theoretical" pressures are identical. At a still higher temperature, the "theoretical" pressure is below the found pressure. The physical meaning of this fact appears to be as follows:—The pressure of a gas depends on the number of molecules present in unit volume, on the average velocity of each molecule, and on the number of impacts on unit area of the surface of the containing vessel in unit time. With constant volume, since the mean distance between the molecules remains constant (on the assumption that the individual molecules are incompressible), the cohesion of the molecules is assumed to be constant. But the rise of pressure produced by rise of temperature of a theoretical gas is based on the assumption that each impact takes place at the centre of each molecule; that is, that the actual volume of the molecules themselves is *nil*. But as this is not the case, as impacts must take place at some distance from the centres of the molecules, they must necessarily be more frequent. The effect of cohesion is to reduce the pressure of the gas, by reducing the average velocity of the molecules, and this, for any given volume, by a constant amount. Hence below a certain temperature the pressure will be less than that of a normal gas, and if the temperature be reduced sufficiently, will become negative. With rise of temperature the average velocity of each molecule will increase at the same rate as in the case of a perfect gas, but the number of impacts, owing to the increased chances of collision, and consequently the pressure, will increase at a greater rate than if the gas were perfect. Hence a temperature will ultimately be reached when the pressure will be as much decreased by cohesion as it is increased by the more frequent encounters of the molecules; and at that temperature the density of the gas will be normal. At still higher temperatures, the pressure, and therefore the value of the expression pt/v, will be greater, and the vapour-density less than that of a perfect gas. That the numerical value of the expression pt/v would ultimately exceed unity has indeed been experimentally proved by Natterer, in his experiments on the compression of the so-called permanent gases, at temperatures far above their critical points.

In conclusion, it is pointed out that the equations of Clausius, van der Waals, and Sarrau do not express the true relation between volume, temperature, and pressure. As before stated, the relation of temperature and pressure to volume is by no means so simple as they represent it to be. W. R.

Compressibility of Solutions of Gases. By F. Isambert (*Compt. rend.*, **105**, 375—377).—All known facts indicate that the solution of a gas in a liquid is a very complex phenomenon, and these experiments were undertaken with a view to throw some light on the problem of the nature of solution. The coefficients of compressibility obtained were as follows:—

Water: —0·0000443 at 20°.

Ammonia (330 litres of gas per litre of liquid): —0·0000381 at 21—22·5°.

Ammonia (140 litres of gas per litre of liquid): —0·0000389 at 20·4—22·2°.

Hydrochloric acid (at 22°): —0·0000366 at 19·6—20·5°.

Alcohol: —0·0001076 at 19°.

Ammonia in alcohol (87 litres per litre): —0·0001071 at 18·0—19·7°.

Sulphurous anhydride in alcohol (60 litres of gas per litre of solution): —0·0001031 at 18·9—20·3°.

Ether: —0·000183 at 21·5°.

Ammonia in ether: —0·000185 at 21—22°.

The solution of hydrogen chloride, which is usually regarded as containing definite hydrates, has a compressibility less than that of water, and in this respect resembles saline solutions. An aqueous solution of ammonia behaves in the same manner. The volume of ammonia dissolved by ether is too small for any conclusion to be drawn from this case, whilst the compressibility of the solution of ammonia in alcohol is practically identical with that of alcohol, and that of sulphurous anhydride in alcohol is slightly lower. The mere dissolution of a gas in a liquid has very little effect on the compressibility of the latter. An aqueous solution of ammonia, however, behaves like a true compound. C. H. B.

Solution. By W. Durham (*Chem. News*, **56**, 152—153).—In this paper the author draws attention to the support the theory, promulgated by him in 1878, receives from the thermochemical results accumulated of late years. According to this theory, dissolution of a substance in a liquid is due to the chemical affinity of the elements of the substance dissolved for the elements of the solvent, hence common salt dissolves in water, on account of the affinity of sodium for oxygen and chlorine for hydrogen; further chemical affinity is not exhausted in all cases of chemical combination, but sometimes sufficient affinity remains to form "solution compounds."

In support of these statements, he points out that as regards chlorides, bromides, iodides, sulphates and nitrates, the available data indicate that the heat of dissolution varies directly; firstly, as the heat of combination of the positive element of the salt with oxygen in water varies; secondly, as the heat of combination of the negative element with the hydrogen varies; but that it varies inversely as the heat of combination of the positive and negative elements of the salt varies. Moreover, when salts differing in heats of combination are dissolved, the heats of dissolution differ to a similar extent, the greatest heat of dissolution being associated with the lowest heat of combination.

The author shows that the absolute amount of heat of dissolution appears to arise from a balancing of affinities among the constituent elements, for instance, when $M,Cl_2 - [M,OAq + \text{Neutr.}] = H_2,Cl_2,Aq - H_2,O$ there is no heat of dissolution, and the salt is not soluble. It also would appear that, in neutralising an oxide by an acid solution, the operation is incomplete as long as the salt remains in solution; positive heat of dissolution indicating that the oxide and acid are not completely decomposed, whilst negative heat would indicate that the salt and water, resulting from the double decomposition, are not completely formed. When both parts are complete there is insolubility. In the case of sulphates, when the heat of combination of the oxide with the sulphuric anhydride is equal to the heat of combination of the metal with sulphur, there is insolubility, but when the former is less than the latter solubility appears. Examples are given in the original paper illustrating all the above statements and deductions. The author suggests that dissolution is probably a periodic function of the elements. D. A. L.

Solution. By S. U. Pickering (*Chem. News*, **56**, 181—182).—The author, commenting on Durham's paper (preceding Abstract), complains of his (Durham's) reasoning in a circle when drawing his conclusions from the thermochemical data. Moreover, the author warns those in search of laws in thermochemistry as to the uncertainty attached to experimental numbers which agree absolutely with or come even within 100 cals. of the theoretical. D. A. L.

Nature of Solution. By S. U. PICKERING (*Chem. News*, **56**, 191—192).—Referring to a recent communication by Nicol (*ibid.*, p. 162), the author states that the hypothesis on which Nicol bases his argument of the vapour-pressures being a measure of the heat of dissolution is a pure assumption, and one for which we have no particle of evidence.

In a few subsequent remarks, he endeavours to clear up some of the points in dispute between himself and Nicol. D. A. L.

Salt Solutions. By C. BENDER (*Ann. Phys. Chem.* [2], **31**, 872—888).—The author describes further experiments on "corresponding" solutions (Abstr., 1885, 12). Tables are given showing the volumes, densities, and coefficients of expansion of solutions containing from 1 to 6 gram-molecules, or half-molecules, of lithium, ammonium, and barium chlorides per litre. By the aid of these and previous tables, the author has determined by trial the strengths of solutions which, when mixed in equal volumes, furnish solutions of which the densities and coefficients of expansion are the means of those of the constituents. The *relative* strengths of corresponding solutions are indicated by the values of the coefficient μ. n = number of gram-molecules or half-molecules per litre—

$NaCl_{\mu = n}$; $KCl_{\mu = n}$; $\frac{1}{2}(BaCl_2)_{\mu = n}$; $NH_4Cl_{\mu =}$ [illegible]n; $LiCl_{\mu =}$ [illegible]n.

Solutions correspond electrically when the means of their specific resistances and conductivities *most nearly* approach the resistances and conductivities of their mixtures in equal volumes. Electrical measurements were made by Kohlrausch's method, and are given in tables for each salt. These solutions contain

$NaCl_{\mu = n}$; $LiCl_{\mu = n}$; $\frac{1}{2}(BaCl_2)_{\mu = n}$; $KCl_{\mu =}$ [illegible]n; $NH_4Cl_{\mu =}$ [illegible]n.

The resistance of a mixture of two solutions is almost always less than the arithmetic mean of the resistances of the separate solutions. For corresponding solutions, the difference is a minimum.

A similarly simple law does not hold for the conductivities of mixtures. Thus solutions of NaCl and NH_4Cl, and of KCl and $\frac{1}{2}BaCl_2$, correspond as regards conductivity in two very different relative states of concentration. The idea of correspondence is therefore based primarily on resistance.

The author answers the objection of Arrhenius (Abstr., 1887, 415), that correspondence is based on a purely arithmetical relation, and points out that this relation is more general, and not more arbitrary, than that on which Arrhenius founds his idea of "isohydric" solutions. Ch. B.

Compressibility of dilute Salt Solutions and of solid Sodium Chloride. By W. C. RÖNTGEN and J. SCHNEIDER (*Ann. Phys. Chem.* [2], **31**, 1000—1005).—Schumann (Abstr., 1887, 696) states that weak solutions of potassium and calcium chlorides at 15°, and of ammonium and strontium chlorides at 0°, are more compressible than pure water. In their previous work (*Ann. Phys. Chem.*

[2], **29**, 165), the authors have not observed such an anomaly. They have therefore repeated Schumann's experiments as nearly as possible, but with entirely opposite results. No details are given.

The authors also state that they have found no perceptible difference between the compressibilities of air-free water and of water saturated with air at ordinary temperature and pressure. The difference, at any rate, is less than 0·2 per cent.

By methods already described, they have also found the relative apparent compressibility of solid sodium chloride = 0·049. This value is not very different from the number 0·044, which is obtained when the interpolation formula for the relative apparent compressibility of sodium chloride solution (*loc. cit.*) is extended beyond the limits of solubility of the chloride, and n put = ∞. It may perhaps be possible in this way from the known compressibility of a solution to calculate, at least approximately, that of the dissolved solid. The above direct determination gives for the true compressibility $5·0 \times 10^{-6}$. By calculation from the interpolation formula, the number $4·8 \times 10^{-6}$, and from the formula for the relative molecular compressibility the number $4·7 \times 10^{-6}$, are obtained.

These numbers differ greatly from that obtained by Braun (Abstr., 1887, 436), namely, $1·4 \times 10^{-6}$. The authors therefore give details of their own experiments. They have further made determinations, using comparatively low pressures, in order to eliminate errors due to inclusion of air in crevices in the crystals. These led to the above number 0·049. Ch. B.

Water of Crystallisation of dissolved Cobalt Salts. By J. KALLIR (*Ann. Phys. Chem.* [2], **31**, 1015—1028).—It is known that the dehydration by heat of cobalt chloride in solution is effected at a lower temperature when the solution is saturated with sodium chloride. The author has studied this reaction quantitatively by observing the accompanying changes in the absorption-spectrum in the neighbourhood of the D line. Let A be the absorption coefficient for a known solution of the hydrated salt of thickness d, E that of the same solution when dehydration is complete, and M the coefficient when at any temperature a fraction $1/x$ has been converted. In the latter case, the absorption will be equivalent to that produced by a thickness d/x of dehydrated solution, and a thickness $d-d/x$ of unchanged solution, whence—

$$M = A^{\left(1 - \frac{1}{x}\right)} \cdot E^{\frac{1}{x}} \text{ and } \frac{1}{x} = \frac{\log M - \log A}{\log E - \log A}.$$

A beam of parallel rays from a petroleum lamp, or from the sun, was directed perpendicularly upon a glass trough with parallel sides containing the solutions under experiment (0·0746 gram of $CoCl_2$ per litre). The coefficients were measured by Glan's photometer (*Ann. Phys. Chem.* [2], **1**, 351; **12**, 481; **14**, 177; and **15**, 337). The conversion was assumed to be complete when rise of temperature caused no further change in the absorption. This occurred at 84° for a saturated salt solution, at 94° when the solution contained 1·12 grams NaCl to 5·22 grams cobalt solution. In any particular solution, the absorption is constant for a given temperature. The trough was heated by means of an air-bath. Curves having the temperatures in degrees as abscissæ, and the percentages of dehydrated salt as ordinates, were then traced for each sodium chloride solution.

These curves show that in each case the dehydration is continuous; no intermediate hydrate is formed. The actual composition of the final salt, $CoCl_2$ or $CoCl_2 + Aq$, is unknown. The rate at which dehydration takes place is more rapid the higher the temperature. At low temperatures, the curves for different salt solutions are congruent; and as a rule, one curve can be converted into another by moving each point of it along the abscissa through a definite number of units. The course of the conversion is thus always the same, and is independent of the amount of cobalt in solution; the presence of sodium chloride simply transfers it to a lower range of temperature. In a pure cobalt chloride solution, the conversion is very slight below 100°.

Experiments were also made with sodium bromide and iodide. The greatest effect is produced by the chloride, the least by the iodide. With the bromide and iodide, the action is not very regular; probably because the *degree* of saturation is lowered as the temperature rises.

Ch. B.

Condensation of Water Vapour by Solid Substances. By T. Ihmori (*Ann. Phys. Chem.* [2], **31**, 1006—1014).—A continuation of previous experiments (Warburg and Ihmori, *ibid.*, **27**, 481). The author has improved the construction of the balance there described, avoiding the use of sealing-wax, which is hygroscopic, and of brass, which becomes so by oxidation. Platinum is used instead.

Sealing-wax, shellac, and metallic surfaces varnished with shellac, are very hygroscopic. Bright metal surfaces take up very little water; but if oxidation occurs, the surface may become rather hygroscopic. Water taken up by such a surface is only partly given off in a dry vacuum.

Agate is also very hygroscopic: the absorption appears to vary with the colour. Rock crystal is very slightly hygroscopic, especially after cleaning with leather, or, still better, washing with hot water. After the latter treatment, the absorption becomes zero or negative.

Platinum condenses water very slightly; the condensation disappears entirely after rubbing with leather. Old platinum may require heating to redness, probably in order to destroy a film of grease.

In the author's opinion, a sensitive balance should have all metallic parts platinised; neither shellac varnish nor agate should be used in its construction; rock crystal might, perhaps, be substituted for the latter. Platinum or platinised brass is preferable to rock crystal for weights.

Experiments with glass are also described. Ch. B.

Rate of Oxidation of Carbon Compounds by Potassium Permanganate. By Dreyfus (*Compt. rend.*, **105**, 523—525).—When the oxidation of carbon compounds by potassium permanganate reaches its limit, the quantities of oxygen absorbed by equal weights of different compounds are not identical, but are of the same order of magnitude. When, however, the action is restrained, and the rate of oxidation is measured, the results vary widely with different compounds.

The reagents employed consisted of a potassium permanganate solution equivalent to a solution of 0·1 gram of crystallised oxalic acid per litre, and a solution of indigocarmine, 10 c.c. of which was equal to 5 c.c. of the permanganate. A 1 per cent. solution of ethyl alcohol was used as a standard liquid, and all the other solutions were compared with it, the rate of oxidation of ethyl alcohol being taken as unity. 50 c.c. of the alcohol solution was placed in a cylinder, and an equal volume of the solution to be examined in another cylinder, 25 drops of sulphuric acid was added to each, and after two minutes 10 c.c. of potassium permanganate. The cylinders were allowed to remain in diffused light at about 15°, and 10 minutes after the permanganate had been added to the alcohol, the latter was run into 10 c.c. of the indigocarmine solution until the colour of the latter changed to yellow. Two minutes later, the other solution was treated in the same way. A simple calculation gives the quantity of oxygen absorbed by each substance under conditions which are strictly comparable, except that the weights of the substances are not identical. The second solution is diluted to a suitable extent, and after two or three comparative experiments, it is easy to calculate the amount of water to be added to the second substance, in order that the quantity of oxygen absorbed may be the same in both cylinders, and from this we get the weight p of the substance which will absorb as much oxygen in a given time as 1 gram of ethyl alcohol. If the two numbers 1 and $\frac{1}{p}$ are not actually proportional to the rates of oxidation of equal weights of the two substances, they are of the same order, and may be regarded as coefficients of the relative rates of oxidation of the various compounds.

A large number of substances were examined, and the rates of oxidation vary from 0·2 in the case of saccharose to 10,000 in the case of pyrogallol; next in order to pyrogallol comes catechol, quinol, and resorcinol, with 5000, 3333, and 2000 respectively, phenol 786·0, α-naphthol 769·00, and β-naphthol 666·0. Hydrocarbons, sugars, alcohols of the ethyl series, and acids of the acetic and benzoic series, have much lower rates, varying from 1·0 to 6·0. Ether and alcohol show identical velocities.

Determinations of the rate of oxidation may be used to determine the class to which a substance belongs, and also to detect impurities in such compounds as acetone. The constitution of compounds affects the rate of oxidation more than their composition. Other conditions being the same, a saturated compound is less active than a non-saturated compound. Substances of the same chemical function show comparable rates of oxidation. The aldehyde function is more active than the alcoholic, and the phenolic function shows a very much greater activity. The rates of oxidation of isomerides are not the same. In the case of the dihydroxybenzenes and the toluidines, the ortho-derivative absorbs the most oxygen, and the meta-derivative the least, the para-derivative occupying an intermediate position.

C. H. B.

Laboratory Fittings. By J. Gibson (*J. Soc. Chem. Ind.*, **6**, 205—211).—The following is a list of fittings and apparatus in use at the new chemical laboratories of the University of Edinburgh:—(1) System of ventilation and fume extraction, the draught being produced by a Blackman air propeller; the great power of the draught has rendered it possible to dispense with draught cupboards almost entirely; (2) draught arrangements on the working tables; (3) utilisation of the draught in connection with steam-baths; (4) arrangement for supplying the laboratories with water at a high and constant pressure; (5) gas, water, and steam supply to a stone table intended for combustion and similar operations; (5) convenient arrangement of draught, gas, and steam supply to a small draught cupboard; (7) new substitute for a sand-bath; (8) improved filtering apparatus; (9) apparatus for preserving gaseous hydrogen sulphide. D. B.

Inorganic Chemistry.

Compound of Iodine with Ammonia. By F. Raschig (*Annalen*, **241**, 253—255).—Iodine absorbs dry ammonia gas, forming a dark-blue liquid; Bineau (*Ann. Chim. Phys.* [3], **15**, 80) assigns to this substance the formula $3NH_3,2I$, but according to Millon (*Annalen*, **62**, 54) iodine absorbs less than half the volume represented by this formula. The author finds that the volume of ammonia absorbed by the iodine varies with the temperature. At 20°, the amount of ammonia absorbed corresponds with Bineau's formula, but at 80° it corresponds with NH_3I, at 0° with $I(NH_3)_2$, and at —10° with $I_2(NH_3)_5$. The liquid is decomposed by water, yielding ammonium iodide and nitrogen iodide, but it dissolves completely in alcohol without undergoing any change. W. C. W.

Method for Decomposing Arsenical Sulphides. By H. Warren (*Chem. News*, **56**, 193—194).—The cobalt speiss or arsenical alloy is digested in hydrochloric acid containing copper nitrate, and after a day or so, the insoluble portions are calcined at a low red heat with plentiful access of air; the calcined mass is then easily dissolved by hydrochloric acid and mixed with the other solution. The copper is separated by means of metallic iron, which also removes some bismuth and arsenic; and the iron and remaining arsenic are precipitated by adding milk of lime. The calcium salts are removed by treatment with sulphuric acid, and the solution containing nickel and cobalt is precipitated by means of sodium carbonate. The precipitate is then suspended in water and chlorine passed to saturation, when the nickel goes into solution, whilst the cobalt remains undissolved. The solution is boiled, and on adding caustic soda the nickel is obtained as hydroxide, which is ignited and reduced in the usual way.

D. A. L.

Zinc Titanates. By L. Lévy (*Compt. rend.*, **105**, 378—380).—When a mixture of 6 grams of titanic oxide, 2·5 grams of zinc oxide, and 5 to 10 grams of anhydrous zinc chloride is heated in a glass tube, the reaction is incomplete, and a violet product is obtained which contains an excess of titanic oxide. With excess of zinc chloride, the product is yellowish. If the mixture is heated in a Perrot's furnace in a crucible brasqued with charcoal and rutile, the zinc chloride volatilises, but if the heating takes place in a long porcelain tube closed at one end, a violet or green, crystalline mass is formed, which contains titanium, zinc, silicon, and potassium.

If a mixture of 7 grams of titanium oxide, 5 grams of zinc oxide, and a small quantity of zinc fluoride, or 7 grams of titanium oxide and 30 grams of zinc fluoride is heated under a thin layer of potassium fluoride in a graphite crucible in a Perrot's furnace for an hour and a half, washed with water, and then treated with concentrated sulphuric acid to remove zinc oxide and titanium fluoride, beautiful violet needles are obtained. With potassium chloride in place of the fluoride, the product is a greenish mass. With a mixture of potassium and sodium chlorides the violet needles are obtained mixed with yellowish needles of potassium titanate. The violet crystals are zinc trititanate, $ZnO,3TiO_2$, a small quantity of the zinc being displaced by iron. They are insoluble in water, alcohol, and ether, are not affected by hot dilute sulphuric, nitric, and hydrochloric acids, nor by boiling concentrated solutions of alkaline hydroxides, but are attacked with difficulty by boiling concentrated sulphuric acid, and are decomposed by fusion with potash. They are infusible before the blowpipe, but change to a greenish mass without loss of weight; sp. gr. at 15° = 4·92. The crystals are not attacked by hydrogen at a red heat, but partially volatilise in a mixture of chlorine and hydrogen chloride. When treated with acidified hydrogen peroxide, the latter acquires a characteristic yellow colour, but decomposition is never complete.

C. H. B.

Electrolytic Method of preparing Metallic Alloys, &c. By H. Warren (*Chem. News*, **56**, 153—154).—The following method is recommended for the preparation of alloys such as phosphor-bronzes, silicides, &c. The metal and substance containing alloying material are placed in a deep, conical crucible, through the bottom of which passes a rod of graphite, extending about one inch within the crucible and protected on the outside by an iron tube. The metal is melted and the graphite put in connection with the negative pole, whilst the molten substance on the surface is connected with the positive pole of a battery of two large ferric chloride cells. In this manner silicon copper and silicon-eisen are easily prepared from potassium silicofluoride and the respective metal; the salt being taken in sufficient quantity to form a molten layer 2 inches deep. By some slight variation in the details, phosphor-bronzes can be produced; moreover, native cryolite can be decomposed in contact with metallic zinc, and on subsequently volatilising the zinc, pure aluminium is obtained. Magnesium, barium, strontium, and calcium have not yielded satisfactory alloys as yet. D. A. L.

Process for obtaining the Rare Earths from the Ceriferous Hainstadt Clays. By J. R. STROHECKER (*Chem. News*, **56**, 175—176). —The author attributes the failure of other chemists to obtain cerium from these clays (compare Abstr., 1886, 678) to the fact that in the presence of more than 0·5 per cent. of iron, the cerium precipitated by oxalic acid and potassium sulphate is much contaminated with iron, the oxide prepared therefrom being so coloured by iron oxide as to be mistaken for that substance. He describes the processes by which he affirms that he has separated the various rare earths from these clays. A. J. G.

Reduction of Aluminium Oxide. By G. A. FAURIE (*Compt. rend.*, **105**, 494).—Two parts of pure finely-powdered aluminium oxide is made into a paste with one part of petroleum or some other hydrocarbon, and then mixed with one part of sulphuric acid. When the mass is homogeneous with a pale yellow tint, and begins to give off sulphurous anhydride, it is wrapped in paper and thrown into a crucible heated to above 800° in order to decompose the hydrocarbon. The compact product thus obtained is powdered and mixed with its own weight of a finely-divided metal, the mixture being then heated to a white heat in a plumbago crucible. The regulus after being allowed to cool is found to contain grains of an aluminium alloy in the midst of a metallic powder.

This method of reduction is applicable to silica, calcium oxide, magnesium oxide, &c. C. H. B.

Halogen Compounds of Gold. By G. KRÜSS and F. W. SCHMIDT (*Ber.*, **20**, 2634—2643).—Experiments made with a view to prepare aurous chloride and bromide by the action of chlorine and bromine respectively on gold, gave negative results. The gold is converted into auric compounds in both cases; it is difficult to complete the reaction. It is suggested that the numbers obtained by Thomsen, pointing to the formula Au_2Cl_4, were obtained from a product from which the adhering chlorine had not been removed. When gold is warmed in bromine vapour, a black compound is formed which decomposes into its constituents when heated at 100°, even when kept in bromine vapour. The product contains a large amount of unattacked gold together with auric bromide. The compound Au_2Br_4 is not formed.

The authors conclude that Thomsen's auro-auric chloride and bromide (this Journal, 1877, ii, 485) do not exist. N. H. M.

Gold Sulphides. By L. HOFFMANN and G. KRÜSS (*Ber.*, **20**, 2704—2710).—Oberkampf believed that he obtained an auro-auric sulphide, Au_2S_2, by heating a solution of auric chloride with hydrogen sulphide, but the product, according to Levol and Fellenberg, had a composition varying between that of Au_2S_2 and Au_2S_3, whilst Schrötter and Priwoznik state that an auro-auric sulphide of constant composition cannot be obtained. These results are probably to be attributed to an incomplete removal, by mere washing on a filter, of sulphur precipitated simultaneously, since the authors find that to remove free sulphur from the precipitate it is necessary to wash the sulphide by decantation with absolute alcohol, anhydrous ether, and carbon bisulphide successively (compare Abstr., 1887, 1019).

When a neutral solution of auric chloride is treated with hydrogen sulphide in the cold until all colour has disappeared from the solution, and the precipitate, after repeated washing with water, is washed by decantation as above, auro-auric sulphide, Au_2S_2, of constant composition is obtained, and the reaction is represented quantitatively by Levol's equation, $8AuCl_3 + 9H_2S + 4H_2O = 4Au_2S_2 + 24HCl + H_2SO_4$. Auro-auric sulphide is a black powder in the dry state, and when moist is also black by reflected light, but in the finely-divided state it transmits light of a reddish-brown colour. On porcelain, it gives a black streak. When heated in a tube, sulphur begins to volatilise at 140°, as sulphurous anhydride, and is completely expelled at 250—270° without the intermediate formation of aurous sulphide. With the exception of aqua regia, auro-auric sulphide is insoluble in all acids. Bromine water gradually converts it, especially on warming, into auric bromide and sulphuric acid. Alkaline monosulphides dissolve it slowly in the cold, but readily on heating, yielding brown solutions which become greenish-yellow when the heating is continued; alkaline polysulphides dissolve it in the cold, and the solutions on heating become brown and eventually yellow; yellow sulphide of ammonium, however, dissolves the compound less readily than the sulphides of the alkalis. Concentrated aqueous potash does not attack it in the cold, but on heating converts it into gold, potassium gold sulphide, and potassium gold oxide. Potassium cyanide dissolves it readily. When heated in a current of oxygen, the sulphide ignites, and is converted into gold and sulphurous anhydride, whilst hydrogen sulphide is formed when the heating occurs in a current of hydrogen.

By fusing gold with potassium pentasulphide, Berzelius states that he obtained a sulphide which he believed to have the composition Au_2S_3, although no analyses were made. The authors have endeavoured to prepare a gold sulphide of this composition in four ways:—(1) By Berzelius' method; (2) by Oberkampf's and by Yorke's method (this Journal, 1848, 236), which consists in precipitating a saturated solution of auro-auric sulphide in sodium bisulphide with an acid; (3) by precipitating a saturated solution of auro-auric sulphide in sodium monosulphide with hydrochloric acid; and (4) saturating a solution of sodium gold oxide with hydrogen sulphide and heating the normal sodium thioaurate with an acid; the precipitates in every case were washed by decantation with alcohol, ether, and carbon bisulphide. The precipitated sulphide obtained by the first two methods, however, contained more sulphur than required for the formula Au_2S_3, and had not a constant composition; whilst that prepared by the last two methods had a composition intermediate between that of Au_2S_2 and Au_2S_3. The authors therefore conclude that auric sulphide, Au_2S_3, does not exist, and show that the properties of the so-called compound are those of a mixture of auro-auric sulphide and sulphur, the latter being left as an insoluble, white powder on digestion with potassium cyanide. W. P. W.

Mineralogical Chemistry.

Cliftonite, a Cubic Form of Graphitic Carbon. By L. Fletcher (*Min. Mag.*, 7, 121—130).—A meteoritic iron found on 5th January, 1884, in the district of Youndegin, Western Australia, contains a remarkable form of carbon resembling graphite but crystallising in the cubic form. Four fragments of the meteorite were found, weighing 25¾, 24, 17, and 6 lbs. respectively. In addition there was about 17 lbs. of what appeared to be an outer shell, doubtless due to the weathering of the original mass. The meteorite is extremely hard, and contains numerous inclusions of schreibersite. It has a sp. gr. of 7·85. No distinct figures were obtained on etching. Analysis gave—

Fe.	Ni.	Co.	Cu.	Mg.	P.	S.	Insol. cubes.	Total.
92·67	6·46	0·55	trace	0·42	0·24	nil	0·04	100·38

The insoluble residue consists of about a hundred small cubes of an opaque greyish-black mineral with metallic lustre. The hardness is 2·5, the sp. gr. 2·12, and the streak black and shining. It is not attacked by acids, and but slowly by fused nitre. It burns away very slowly in air, leaving a minute residue. Chemical tests show that the residue resembles graphite, but it is harder and occurs in definite cubic crystals. The author is of opinion that it is an allotropic modification of carbon distinct from diamond and graphite, and names it *cliftonite* after Professor R. B. Clifton, of Oxford. B. H. B.

Natural Gas of Pennsylvania. By K. Sorge (*Jahrb. f. Min.*, 1887, ii, Ref., 318—320; from *Stahl und Eisen*, 7, 93—108).—Since 1821, natural gas has been used in Pennsylvania in a limited and irregular way for illuminating and heating purposes. Since 1883, however, it has attained an extraordinarily rapid development for industrial purposes. At the present time, 15 towns are supplied with natural gas.

The chemical composition of the gas varies in the different wells, and even in the same well after a short lapse of time. In all cases, marsh-gas is the principal constituent. The mean volumetric composition of the gas is as follows:—

CH_4.	H.	O.	N.	C_2H_6.	C_2H_4.	CO_2.	CO.	Total.
67	22	0·8	3	5	1	0·6	0·6	100·0

The composition is said to vary within the following limits:—

CH_4.	H.	N.	C_2H_6.	C_3H_8.	CO_2.	CO.
60—80	5—20	1—12	1—8	0—2	0·3—2	trace

Experiments made by Ford show that gas from the same well may vary considerably. In the gas-pipes of the Edgar Thomson steelworks at Pittsburgh, on different days, the gas contained per cent. :—

Nitrogen.	Carbonic anhydride.	Oxygen.
0 to 23	0 to 2	0·4 to 4

The natural gas of Pennsylvania is strikingly similar in composition to the illuminating gas obtained from Westphalian gas-coal.

B. H. B.

Servian Coal. By S. M. Losanitsch (*Ber.*, **20**, 2716—2718).—Large coal seams occur in Servia in strata varying in age from that of the carboniferous to that of the tertiary formations, and in the paper, analyses are given of graphite, of 33 specimens of coal, and of 4 specimens of shale yielding paraffin, obtained from different localities. Corrections are applied for the amount of hygroscopic water and of ash in the estimation of the percentage of volatile matter and coke obtained from each sample of coal. The table (p. 32) gives the percentage composition of the samples of coal from each formation yielding the greatest and least number of calories respectively.

On dry distillation, the paraffin shale from Subotinci gave the following results:—Tar, 34·00; water, 8·00; ash, 29·25; carbon (in the ash), 17·28; gas, 11·47. A poorer specimen gave 10 per cent. of tar, and the shale from Mijonica, from Orašac, and from Bovan, gave 7 to 18 per cent., 31·5 per cent., and 30 per cent. of tar respectively.

W. P. W.

Ullmannite from Lölling and from Sarrabus. By C. Klein and P. Jannasch (*Jahrb. f. Min.*, 1887, ii, Mem., 169—173).—The ullmannite, NiSbS, discovered at Sarrabus in Sardinia in 1883, crystallises in the regular system in hemihedral crystals with parallel faces. A comparison of this mineral with the hemihedral crystals with inclined faces, having the same empirical constitution, had previously not been instituted. The authors having secured some of the extremely rare material from Lölling, have now been enabled to make the comparison.

The percentage compositions of the ullmannites analysed were as follows:—

	S.	Sb.	As.	Ni.	Co.	Fe.	Insoluble.	Total.	Sp. gr.
I.	14·69	55·71	1·38	28·13	0·25	0·09	0·27	100·52	6·625
II.	14·64	55·73	0·75	28·17	trace	0·17	0·11	99·57	6·733

I. Ullmannite from Lölling; II. from Sarrabus.

It is thus evident that the two specimens have the same chemical composition and specific gravity. Crystallographical investigations, however, prove that the Lölling crystals are hemihedral with inclined faces, whilst the Sarrabus crystals are hemihedral with parallel faces. The authors are unable to prove that these differences are only apparent, and that the crystals are tetartohedral.

B. H. B.

Bismuthite from the Transvaal. By H. Louis (*Min. Mag.*, **7**, 139—140).—Bismuthite occurs plentifully, though finely disseminated,

Description and source.	Locality.	C.	H.	O (& N).	H_2O.	Ash.	Volatile matter.	Coke.	Calories.
Graphite	Stol	92·59	—	—	0·46	6·95	—	—	—
Coal (3) from carboniferous formations	Mustapić-Mišljenovac	82·61	3·99	6·48	0·95	5·96	17·17	75·92	7725
	Kladurovo	74·34	3·69	4·80	1·12	16·77	—	—	7007
Coal (6) from Jura formations	Prljita	86·42	3·81	4·06	1·18	4·53	10·94	83·35	8089
	Milanovac donji	64·54	3·40	11·04	1·80	19·20	17·23	61·77	5845
Coal (12) from chalk formations	Mrtvica	63·42	4·60	18·55	6·10	7·33	37·12	49·45	5771
	Jelovac	51·75	3·47	21·39	13·08	10·31	37·02	39·59	4257
Coal (12) from tertiary formations.	Miliva	59·44	4·14	24·73	10·33	1·36	40·70	47·61	5158
	Kostolac	43·45	3·10	19·19	24·93	8·71	39·61	27·65	3497
Paraffin shale	Subotinci	47·23	6·80	12·13	3·90	29·94	49·36	16·80	5541
	Mijonica	17·09	2·82	12·60	1·70	66·23	29·61	2·48	—

in the auriferous quartz veins in the Lydenburg district of the Transvaal. It is amorphous, pulverulent, opaque, and of a yellow colour. Its hardness is about 3, and its sp. gr. 6·86. Analysis gave the following results:—

Quartz.	Bi_2O_3.	CO_2.	H_2O.	Fe_2O_3.	Total.
0·9	79·6	7·2	2·7	9·6	100·0

This corresponds with the formula $Bi_2H_2CO_6$. A similar paragenesis of bismuthite with auriferous quartz has been recorded from South Carolina. B. H. B.

Barytes in the Carpathians. By F. v. Hauer (*Jahrb. f. Min.*, 1887, ii, Ref., 284; from *Verh. d. geol. Reichsanst.*, **18**, 387).—About three-quarters of a mile to the north-west of Losoncz, an extensive deposit of barytes has been found in association with the melaphyre which bursts through the new red sandstone at that locality. The mineral exhibits a coarsely crystalline texture, and has a sp. gr. of 4·47. Fully developed crystals are not found. B. H. B.

Identity of Dreelite and Barytes. By A. Lacroix (*Jahrb. f. Min.*, 1887, ii, Ref., 266; from *Bull. Soc. Franc. Min.*, **8**, 435—437).—The mineral termed dreelite by Dufrénoy is shown by the angles of the cleavage planes and by the optical characters to be identical with barytes. On account of deficiency of material, an analysis was impossible. Probably, however, the percentage of calcium sulphate given by Dufrénoy was due to impurities. B. H. B.

Titanite. By K. Busz (*Jahrb. f. Min.*, **5**, Beilage, 330—380).—This elaborate monograph is divided into two parts, one giving the results of a chemical and optical examination of a large number of specimens of titanite, the other giving the results of the crystallographical examination. The research was undertaken primarily to determine whether there is any relation between the chemical composition of titanite and its optical constants. The specimens examined were from the following 10 localities:—Schwarzenstein in the Zillerthal, Eisbruckalp, Val Maggia, St. Gothard, Wildkreuzjoch in Tyrol, Laacher See, Arendal in Norway, Renfrew and Grenville in Canada, and Monroe in Michigan. As a rule, the author finds that in titanites containing iron, the angle of the optic axes is larger than that of titanites containing no iron. Exceptions to this rule are, the titanite from Monroe, which with a very high percentage of iron has a comparatively small axial angle, and the titanite from the Zillerthal, which with 1·07 per cent. of ferric oxide has the smallest axial angle of all the titanites examined. It is, however, evident that the magnitude of the axial angle of titanites rich in iron is not in proportion to the percentage of iron.

In his crystallographic investigation, the author observed 75 planes occurring on titanite crystals. Of this number, 22 have not hitherto been observed. B. H. B.

Palæopicrite of Amelose and the Products of its Alteration. By R. BRAUNS (*Jahrb. f. Min.*, 5, Beilage, 275—329).—Since 1831, when Breithaupt first showed that the well-known crystals found at Snarum, Norway, were pseudomorphs of serpentine after olivine, the alteration of olivine and the new minerals formed thereby have frequently been the objects of careful investigation. In no place, however, is the immediate connection of olivine with the products of its alteration so apparent as at Amelose, near Biendenkopf, in Hesse, where within an area of a hundred square yards is found not only the olivine rock in place, but also all the recent minerals formed from it. The latter include serpentine, chrysotile, metaxite, picrolite, a new magnesium iron silicate, calcite, and quartzite interesting on account of the occurrence of the extremely rare planes $\frac{3}{4}R\frac{3}{2}$, $\frac{5}{6}R\frac{5}{4}$. The matrix of these minerals differs from that of most serpentines in that it is of Devonian age, and not interstratified in crystalline schists. It is, in fact, an olivine-diabase (palæopicrite).

The new mineral is named by the author *webskyite*, after the late Professor Websky of Berlin. It is amorphous, and has a pitch-black colour with a brownish-green streak. In thin fragments, the colour is bright green. The hardness is 3, and the sp. gr. only 1·771. Its constituents are qualitatively the same as those of serpentine. Its quantitative composition, however, is different, since it contains 31 per cent. of water, 21 per cent. of which is lost at 100°. Analysis shows that the mineral has the formula $H_6R_4Si_3O_{13} + 6H_2O$, in which R represents Mg and Fe. The new mineral is probably of more frequent occurrence than might be imagined; the author having discovered it on specimens of diopside and of serpentine in the Berlin and Marburg museums. B. H. B.

A Variety of Granulite, the Matrix of two New Minerals. By H. SAUER (*Jahrb. f. Min.*, 1887, ii, Ref., 295; from *Zeit. deutsch. geol. Ges.*, 38, 704—706).—In a new quarry by the railway station of Waldheim in Saxony, the following two new minerals were found in the granulite:—*Prismatine*, crystallising in rhombic prisms without terminal planes, grouped radially. It resembles andalusite or sillimanite. Its composition is given under I. It easily alters to a finely fibrous substance, termed *cryptotile* (Analysis II):—

	SiO_2.	Al_2O_3.	FeO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	30·89	43·06	6·28	15·08	2·04	0·79	1·36	99·50
II.	48·43	41·63	—	2·13	—	—	7·70	99·89

B. H. B.

Rocks from the Congo. By C. KLEMENT (*Jahrb. f. Min.*, 1887, ii, Ref., 300—301; from *Tschermak Min. Mitth.*, 8, 1—27).—The author gives analyses of two specimens of laterite from the Congo. They are composed of a conglomerate of quartz grains cemented by a brown to yellowish-red material. The red rock (I) is more porous than the brown (II), and seems to be a product of the decomposition of the latter. These laterites are said to be a detritus of the crystalline schists in the interior of the continent. For the analyses, the material was freed from the coarsest quartz grains.

	SiO_2.	P_2O_5.	SO_3.	Cl.	Fe_2O_3.	FeO.	Al_2O_3.	CaO.	MgO.
I.	52·91	0·51	0·29	0·08	36·26	0·29	4·13	0·19	0·07
II.	63·08	1·22	0·27	0·13	27·65	0·52	2·30	0·57	0·41

	Na_2O.	K_2O.	H_2O.	Total.
I.	0·08	0·04	6·16	101·01
II.	0·19	0·06	4·71	101·11

B. H. B.

The Water Supply of Oderzo. By M. Spica and G. Halagian (*Gazzetta*, **17**, 317—323).—The water supply of the municipality of Oderzo is taken from three mountain springs, Monticano, Lia, and Navisego, which pass through a clay soil. The analyses tabulated below show that these waters are of the highest order of purity. The colour viewed through a tube was a pale-yellow. With an alcoholic solution of tannin (Hager's test), they remained perfectly clear for several days. With phenolphthaleïn, they showed no reaction, but with litmus they appeared slightly alkaline.

Results of Analyses expressed in grams per litre.

	Monticano.	Lia.	Navisego.
Total residue	0·31	0·287	0·289
Chlorine	0·00797	0·00206	0·00197
Sulphuric anhydride	0·02782	0·04703	0·04446
Silica	0·001	0·00425	0·0028
Ferric oxide and alumina	0·0015	0·00125	0·003
Lime	0·08888	0·09188	0·09632
Magnesia	0·06036	0·03081	0·03099
Nitric acid		very slight traces	
Organic matter	0·02136	0·01583	0·01939
Oxygen required for organic matter	0·00108	0·0008	0·00098
Total carbonic acid	0·2064	0·168	0·175
Free carbonic acid	0·1004	0·0841	0·0858
Total hardness, French scale	24°·0	23°·5	27°·0
Permanent „ French scale	12°·0	12°·4	13°·0

V. H. V.

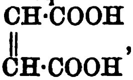
Organic Chemistry.

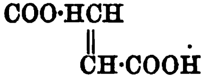
Arrangement in Space of the Atoms in the Molecules of Carbon-compounds. By J. Wislicenus (*Chem. Centr.*, 1887, 1005—1009).—Van't Hoff and Le Bel were the first to explain the optical difference of certain carbon-compounds by a difference in the relative arrangement of the atoms in space within the molecule; since their work, however, no serious attempt has been made to apply their theory to explain the isomerism of certain compounds, whose composition, according to present views, is identical.

Such peculiar cases as those established by the researches of Fittig on the isomerism of maleïc and fumaric acids, however, and the discovery of a third and fourth monobromocinnamic acid, have been classified under the generic term of alloisomerism. Chemists hitherto seem to have contented themselves with a name.

Adopting the hypothesis of van't Hoff and Le Bel that the atoms occupy the solid angles of a tetrahedron, being arranged around a central carbon-atom it is evident that two carbon-atoms, associated together in the paraffinoïd form of combination, would revolve around one common axis, passing through the point of union of the atoms and the direction of attraction of two associated atoms, such as those of hydrogen. When two carbon-atoms are combined together, as in the olefines, they can only revolve round an axis which is the straight line connecting the two common carbon-atoms.

Supposing all four of the affinities of the saturating atoms are unequal, then six isomerides are possible, in the case of two pairs three isomerides, and three also if two affinities are equal and two unequal. For maleïc acid, van't Hoff has proposed the formula $\begin{array}{l}\mathrm{CH{\cdot}COOH}\\ \|\\ \mathrm{CH{\cdot}COOH}\end{array}$, so that for fumaric acid the formula will be





$$\begin{array}{l}\mathrm{COO{\cdot}HCH}\\ \qquad\qquad\|\\ \qquad\qquad\mathrm{CH{\cdot}COOH}\end{array}.$$

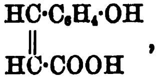
In order to explain the conversion of maleïc into fumaric acid through the intervention of halogen-derivatives of succinic acid, it is supposed that the atoms combined with neighbouring carbon-atoms mutually react on one another according to their chemical affinity. Hence, it follows that two carbon-atoms combined together by one affinity, and being in a position by revolution around their axis to give way to this attraction, will so arrange themselves that the associated radicles interchange positions in the system. Such a relative arrangement will be stable in the cold, but at a higher temperature, as the interoscillation of the elements will be more frequent, there is a loosening of the affinities, and a different configuration ensues. When an unsaturated compound passes into one that is saturated, it is indifferent to which of the two carbon-atoms each particular radicle attaches itself; the compounds formed are identical. But if an atom is combined with two different radicles, then by addition an asymmetrical carbon-atom results according as the added atoms attach themselves to one or other position of affinity. This explains the formation of optically inactive compounds under these conditions, since both modifications are produced in equal quantities.

As regards the nomenclature of these different geometrically isomeric configurations, it is proposed to call the arrangement $\begin{array}{l}aCb\\ \|\\ bCa\end{array}$ the centrally or axially symmetrical, and the arrangement $\begin{array}{l}aCb\\ \|\\ aCb\end{array}$ the plane symmetrical.

The following examples are given in illustration of the above views:—Tolane dichloride exists in two modifications; according to the author's hypothesis, the modification of higher melting point, obtained by the direct chlorination of tolane, is the plane symmetrical $\begin{array}{l}\mathrm{Ph{\cdot}C{\cdot}Cl}\\ \;\;\|\\ \mathrm{Ph{\cdot}C{\cdot}Cl}\end{array}$, whilst the other is the axially symmetrical $\begin{array}{l}\mathrm{Ph{\cdot}C{\cdot}Cl}\\ \;\;\;\;\|\\ \mathrm{Cl{\cdot}C{\cdot}Ph}\end{array}$. As fumaric acid is principally formed by heating malic acid, in which, doubtless, the carboxyl-group has more inclination towards the hydrogen-atom than to the hydroxyl- or other carboxyl-group, its constitution may be represented by a configuration $\begin{array}{l}\mathrm{COOH{\cdot}CH{\cdot}OH}\\ \;\;\;\;\;\;|\\ \mathrm{HH{\cdot}C{\cdot}COOH}\end{array}$, from which by the abstraction of a molecule of water the formula $\begin{array}{l}\mathrm{COOH{\cdot}CH}\\ \;\;\;\;\;\;\|\\ \;\;\;\;\mathrm{HC{\cdot}COOH}\end{array}$ results. The conversion of ethyl maleate into ethyl fumarate by iodine is explained by the intermediate formation of diiodosuccinnic acid, an interchange of position of the iodine- and hydrogen-atoms; the removal of a molecule of hydrogen iodide gives ethyl iodofumarate, which in its turn is reduced by the hydrogen iodide to ethyl fumarate.

The reverse process of conversion of fumaric into maleïc acid through the intervention of dibromosuccinic acid can be explained in like manner. The isomerism of crotonic and isocrotonic acid is also of a similar order, the constitution of the one being expressible by a formula $\begin{array}{l}\mathrm{H{\cdot}C{\cdot}Me}\\ \;\;\;\|\\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$, of the other as $\begin{array}{l}\mathrm{Me{\cdot}C{\cdot}H}\\ \;\;\;\;\;\|\\ \;\;\mathrm{H{\cdot}C{\cdot}COOH}\end{array}$. Cinnamic acid should also exist in two geometrically isomeric forms, of which, as yet, only one has been obtained.

β-Coumaric acid has the plane symmetrical arrangement



$$\begin{array}{l}\mathrm{HC{\cdot}C_6H_4{\cdot}OH}\\ \;\;\|\\ \mathrm{HC{\cdot}COOH}\end{array},$$

as it is easily converted into its lactone, coumarin; in its isomeride, the atoms are arranged in the axially symmetrical configuration; this, by fuming hydrobromic acid, is converted into coumarin, by temporary addition of a molecule of the acid, and by an inclination towards formation of the lactone.

By this theory, the removal of the elements of a halogen acid and simultaneously of carbonic anhydride from the sodium salt of a *β*-halogen substituted acid is explained, as also the formation of anhydrides and lactones when two carboxyl- or a hydroxyl- and carboxyl-group are in the γ-position.

The author is engaged on experimental evidence in favour of this theory. V. H. V.

Nitrosates, Nitrosites, and their Derivatives. By O. WALLACH (*Annalen*, **241**, 288—315).—The crystalline compound which Guthrie

(*Annalen*, **116**, 248; **119**, 84) obtained by the direct union of amylene with nitrogen peroxide, is most conveniently prepared by passing the nitrous fumes evolved by the action of strong nitric acid on arsenious oxide into a well-cooled mixture of amylene (1 vol.) and glacial acetic acid (2 vols.). The operation is interrupted when the colour of the liquid changes from blue to green. The crystals are washed with acetic acid, afterwards with water. As commercial amylene is a mixture, the product is not homogeneous. On recrystallisation from chloroform or benzene, two substances having the composition $C_6H_{10}N_2O_4$ are deposited, namely, cubes melting at 96—97°, and needles melting at 89°. This compound is not a dinitrite but a nitroso-nitrate or *nitrosate*. On boiling with alcohol and aniline, it yields aniline nitrate and *amylenenitrolaniline*, $NHPh{\cdot}C_5H_9{:}NOH$. The base melts at 140—141°. It dissolves freely in ether, chloroform, warm alcohol, and in dilute acids, and crystallises well. The *hydrochloride*, $C_{11}H_{16}N_2O,HCl$, is deposited from a hot aqueous solution in anhydrous crystals. It is best prepared by passing hydrogen chloride into an ethereal solution of the base, when the hydrochloride is precipitated in the form of a crystalline powder. The *nitroso*-compound, $NO{\cdot}NPh{\cdot}C_5H_9{:}NOH$, is deposited as a crystalline powder when a solution of sodium nitrite is poured into an acid solution of the base. It melts at 127—128°, and is soluble in alcohol and in alkalis. The nitroso-compound is reprecipitated on adding an acid to the alkaline solution. The hydrochloride is decomposed by boiling with water, or better with hydrochloric acid, yielding hydroxylamine and a ketone base, $NHPh{\cdot}C_5H_9{:}O$. The new base melts at 61°, and is soluble in alcohol, ether, and in hot water.

Amylenenitrolparatoluidine, $C_{12}H_{18}N_2O$, and its hydrochloride and nitrate form well-developed crystals. The base melts at 111—112°, and the nitroso-derivative at 147—148°. The hydrochloride is decomposed on boiling it with hydrochloric acid, yielding hydroxylamine and the base $C_{12}H_{18}N_2O$ melting at 98°.

Amylenenitrolorthotoluidine melts at 115°. The nitroso-derivative melts with decomposition at 149—150°. The hydrochloride is more soluble in water than the corresponding para-salt.

Amylenenitrolorthoanisidine melts at 138—139°. The hydrochloride is deposited from its aqueous solution in prisms. Amylene nitrosate and piperidine act on each other very energetically, forming a crystalline base, $C_{10}H_{20}N_2O$. It melts at 95—96°, and is insoluble in water and in alkalis. The salts dissolve freely in water. The hydrochloride is an oily liquid, but the platinochloride $(C_{10}H_{20}N_2O)_2,H_2PtCl_6$, forms beautiful prisms. *Amylenenitroldiethylamine* crystallises in plates and melts at 71—72°. *Amylenenitrolallylamine* is soluble in water. The hydrochloride, $C_8H_{16}N_2O,HCl$, is crystalline. This base is isomeric with nitrosoconiine.

Amylene nitrosate acts on sodium ethoxide, forming a crystalline compound which melts at 100°, and also on ethyl acetoacetate, yielding a crystalline compound of the composition

$$C_5H_{10}NO{\cdot}CH(COMe){\cdot}COOEt.$$

Guthrie (*loc. cit.*) observed that amyl nitrosate acts on potassium cyanide, but the author finds that a crystalline compound and potassium nitrate, not a liquid and a *nitrite*, are formed in the reaction.

A blue crystalline compound is formed by passing nitrous fumes into bromamylene dissolved in acetic acid, and pouring the crude product into water. This compound acts on piperidine at the ordinary temperature, yielding a colourless, crystalline substance which exhibits neither acid nor basic properties. It is soluble in alcohol, is rich in bromine, and has an odour resembling that of camphor.

W. C. W.

Synthetical Experiments in the Sugar-group. By E. Fischer and J. Tafel (*Ber.*, **20**, 2566—2575).—It was previously shown (Abstr., 1887, 651) that acraldehyde bromide is converted by baryta into what is probably a glucose. With phenylhydrazine, the product of the reaction yields *α*- and *β*-phenlylacrosazones, melting at 205° and 148° respectively.

When isoglucosamine oxalate (Fischer, Abstr., 1886, 934) is dissolved in ice-water (10 parts) and treated with sodium nitrite, an evolution of nitrogen takes place; after three hours, the temperature is allowed to rise to 20°. The product is exactly neutralised with aqueous soda, evaporated in a vacuum, and the residue extracted with absolute alcohol. On evaporating the solution, levulose is obtained as a yellowish syrup; the spec. rotatory power at 80° = 25°. It produces strong fermentation with yeast in 10 minutes, gives a precipitate of phenylglucosazone with phenylhydrazine, and yields Kiliani's levulose hydrocyanide when treated with hydrocyanic acid. The constitution of isoglucosamine is probably $NH_2{\cdot}CH_2{\cdot}CO{\cdot}[CH(OH)]_3{\cdot}CH_2{\cdot}OH$. Ledderhose's isomeric glucosamine has possibly the constitution $CHO{\cdot}CH(NH_2){\cdot}[CH(OH)]_3{\cdot}CH_2{\cdot}OH$.

α-Phenylacrosazone is obtained in the following manner: A solution of 75 grams of pure, crystallised barium hydroxide in 1·25 litre of water is cooled with ice-water; 50 grams of freshly-distilled acraldehyde bromide is then added by drops, the baryta solution being kept violently shaken. Eight preparations are united, made slightly acid with sulphuric acid, and treated with a strong solution of sodium sulphate until the barium is completely precipitated. After 12 hours, it is filtered, neutralised with aqueous soda, and evaporated in a vacuum to 1½ litre. When cold, a solution of phenylhydrazine hydrochloride (50 grams) and sodium acetate (50 grams) in 100 c.c. of water is added, and the whole left for 12 hours; it is then filtered and warmed on a water-bath with 150 grams more of phenylhydrazine hydrochloride and 150 grams of sodium acetate. In the course of four hours, a half crystalline and half resinous precipitate separates; this is washed with water and extracted with ether, when the greater part of the resin and the *β*-phenylacrosazone dissolves, leaving the *α*-phenylacrosazone. After filtration, the *α*-compound is repeatedly extracted with boiling alcohol, and treated with hot water, after which it is almost pure. The yield from 400 grams of bromide is 18 grams. It melts at 205° (uncorr.), and is very sparingly soluble. On adding water to the hot alcoholic solution, it separates in long, slender needles.

α-Acrosamine, $C_6H_{13}NO_5$, is prepared similarly to isoglucosamine (*loc. cit.*) by reducing the acrosazone with zinc-dust and acetic acid, and is purified by means of the oxalate. It shows all the reactions of the glucosamines. When the oxalate is dissolved in ice-water and treated with sodium nitrite, *α-acrose*, $C_6H_{12}O_6$, is formed; this is obtained as a light-brown syrup, having a sweet taste. It reduces Fehling's solution.

β-Phenylacrosazone, $C_{18}H_{22}N_4O_4$, is obtained by evaporating its ethereal extract (obtained in the purification of the α-compound), dissolving in alcohol, and precipitating with water. The dried product is exhausted with cold benzene several times. The yellow crystalline residue is boiled with acetone (2 parts), filtered, and precipitated with ether and light petroleum. It crystallises in slender, yellow needles melting at 148°, dissolves in alcohol and acetone much more readily than the α-compound, but is almost insoluble in ether when pure. The yield is small.

The resemblance of α-phenylacrosazone to phenylglucosazone makes it probable that α-acrose has the constitution expressed by the formula $OH{\cdot}CH_2{\cdot}[CH(OH)]_4{\cdot}CHO$; the constitution of β-acrose would then be $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}C(OH)(CH_2{\cdot}OH){\cdot}CHO$ or

$$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO{\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

The lower melting point and more ready solubility of the β-osazone point to its being a derivative of a sugar with an abnormal carbon-chain.

Isodulcitolphenylhydrazine, $C_6H_{12}O_4{:}N_2HPh$, crystallises from alcohol in colourless plates melting at 159°. It is insoluble in ether, readily soluble in water and in alcohol. The aqueous solution is dextrorotatory.

Lactosephenylhydrazine, $C_{18}H_{28}O_{10}N_2$, is prepared by adding phenylhydrazine (1 part) to a solution of milk-sugar (2 parts), in hot water (2 parts). After two days, twice the volume of absolute alcohol is added, and the whole treated with much ether. The syrupy precipitate after being repeatedly dissolved in alcohol and precipitated with ether, is obtained as a solid mass. It is filtered, quickly washed with ether, and dried in a vacuum over sulphuric acid. It dissolves readily in water and in alcohol, and is insoluble in ether. It is lævorotatory.

N. H. M.

Isonitrosogalactose. By P. RISCHBIETH (*Ber.*, **20**, 2673—2674).—When galactose (1 gram) and hydroxylamine hydrochloride (0·4 gram) are dissolved in a small quantity of water, treated with sodium carbonate (0·65 gram), and allowed to remain for 24 hours, *isonitrosogalactose*, $C_6H_{12}O_5{:}NOH$, is obtained as a colourless, crystalline substance which melts at 175—176°, and is readily soluble in hot water, soluble in hot dilute alcohol, and practically insoluble in ether and absolute alcohol. Under similar conditions, no separation could be obtained from dextrose, levulose, or arabinose.

W. P. W.

The Carbohydrate Character of Formose. By C. WEHMER (*Ber.*, **20**, 2614—2618).—Plants which readily produce starch from dextrose, cane-sugar, mannitol, and glycerol, do not produce starch in any determinable amount from formose.

When 28 grams of formose syrup is boiled with 100 c.c. of water and 5 grams of hydrochloric acid (sp. gr. 1·2) for 11 hours, a separation of humic substance (3·5 grams) takes place. The filtrate shows the iodoform reaction distinctly and reduces Fehling's solution. No levulinic acid is formed. 13 per cent. phosphoric acid produced the same decomposition, also without formation of levulinic acid.

The author concludes that formose is not a carbohydrate.

N. H. M.

Saccharification in Vegetable Tissues. By BONDONNEAU and FORET (*Compt. rend.*, **105**, 617—618).—The amylaceous plant is heated at 90—100° with acid of 1 to 2 per cent., and the starch is gradually and completely converted into dextrin, glucose, saccharose, &c., and the soluble products thus formed diffuse through the cell-walls into the surrounding liquid. When the proportion of sugar in the liquid ceases to increase, the process is finished. This method is readily applied on a large scale. The exhausted pulp is free from starch, but constitutes a valuable nitrogenous food-stuff for cattle. The pulp from maize has the composition,—Water, 79·15; ash, 1·22; nitrogenous matter, 8·38 (containing nitrogen, 1·31); oil, 5·48; cellulose and loss, 5·77 = 100. It will be observed that water has been substituted for the starch.

C. H. B.

Amines of the Paraffin and Benzene Series. By MALBOT (*Compt. rend.*, **105**, 574—576).—In the reactions described, unless otherwise stated, the substances were mixed in equal molecular proportions.

Ethylamine and aqueous ammonia at 100° yield triethylamine, but at 150° tetrethylammonium chloride is obtained in considerable quantity. Propyl iodide under the same conditions yields tripropylamine at 100°, and tetrapropylammonium iodide at 150°. Although pure tripropylamine combines but slowly with propyl iodide in the cold, combination becomes complete at 150°. Tripropylamine has no action on propyl chloride in the cold, and the reaction takes place slowly at 150°, but becomes very rapid at 190°, the products being tripropylamine and dipropylamine hydrochlorides and propylene. Butyl iodide and aqueous ammonia at 160° yield only tributylamine, and the action of tributylamine on butyl iodide is strictly analogous to that which takes place with the corresponding propyl-derivatives. Tributylamine acts slowly on butyl chloride at 80°, but at 170° pure dibutylamine hydrochloride and butylene are obtained. Dibutylamine and butyl iodide in the cold yield dibutylamine hydriodide and free tributylamine; at a higher temperature, the reaction is analogous to that obtained with the chloride.

Isoamyl iodide and aqueous ammonia at 150° yield tetramylammonium iodide. Triamylamine acts slowly on amyl iodide in the cold, but at 150° triamylamine hydriodide and amylene are formed. At 200°, the reaction is very rapid, and the products are diamylamine hydriodide and amylene. With amyl chloride, a salt of triamylamine is formed at 170°, and undergoes no further alteration even at 210°. Diamylamine and amyl iodide yield diamylamine hydriodide, free triamylamine, and tetramylammonium iodide.

Capryl chloride with aqueous ammonia in equal molecular proportions at 170° yields monocaprylamine together with a small quantity of the diamine and caprylene. With twice the proportion of ammonia, the diamine is the chief product, and no caprylene is formed. Capryl iodide with an equivalent quantity of ammonia at 160° yields only monocaprylamine, either free or together with caprylene, the latter occupying at 120° a volume equal to half the volume of capryl iodide used.

Benzyl and metatolyl chlorides yield the tertiary amines almost exclusively, whilst cinnamyl chloride yields the secondary amine. The bases are obtained in the form of salts by the action of the corresponding alcoholic chlorides. The formation of a bivalent hydrocarbon is especially marked with styrolylamines, cinnamene being obtained in large quantity. It is identical with the synthetical cinnamene of Berthelot, and part of it is obtained in the form of metacinnamene.

Whether the products of these reactions are in the free state or in the form of salts is determined by the conditions of equilibrium between the rival attractions of the ammonia and the amines for the ethereal salt which is present, and the acid contained in this salt. The increasing complexity of the amines is the result of a series of successive transformations, a bivalent hydrocarbon being produced simultaneously. This last fact is in favour of the ethylene theory of the constitution of amines. C. H. B.

Allyl-diguanidine and its Derivatives. By A. Smolka (*Monatsh.*, 8, 379—390).—*Allyldiguanidine copper sulphate*, $(C_5H_{10}N_5)_2Cu,H_2SO_4$, is obtained by dissolving dicyandiamide in aqueous copper sulphate and adding allylamine; the mixture is then heated for some hours at 100°. This salt is more soluble in alkaline solutions than in pure water; it separates from boiling solutions in carmine-red, anhydrous crystals, from cold solutions in pale rose-coloured, microscopic needles with 1 mol. H_2O. The other salts were made from the foregoing by double decomposition. The *chloride*, $(C_5H_{10}N_5)_2Cu,2HCl + 2H_2O$, yields groups of rose-red crystals easily soluble in water to an amethyst-coloured solution. The *nitrate*, $(C_5H_{10}N_5)_2Cu,2HNO_3$, forms dark-red crystals easily soluble in water. Other salts were prepared. Copper-allyldiguanidine, $(C_5H_{10}N_5)_2Cu$, was obtained by precipitating a boiling solution of the sulphate with soda. It crystallises in dark rose-red needles, sparingly soluble in cold, more soluble in boiling water. A solution of this base precipitates metallic hydroxides from solutions of metallic chlorides, the chloride described above remaining in solution. When heated above 130°, the base decomposes.

Allyldiguanidine sulphate, $(C_5H_{11}N_5)_2,H_2SO_4 + \frac{1}{2}H_2O$, was obtained by the action of hydrogen sulphide on the copper salt suspended in water. It crystallises in prisms, and is soluble in water, insoluble in alcohol. The *acid sulphate*, $C_5H_{11}N_5,H_2SO_4 + \frac{1}{2}H_2O$, crystallises in scales. The *chloride*, $C_5H_{11}N_5,HCl$, yields transparent prisms easily soluble in water and alcohol. It yields no precipitate with $PtCl_4$, nor with potassium tartrate. The *acid chloride*, $C_5H_{11}N_5,2HCl$, forms small, transparent prisms easily soluble in water and alcohol. *Allyldiguanidine*, $C_2H_6N_5 \cdot C_3H_5$, was prepared by treating a solution of the sulphate with the calculated quantity of barium hydroxide and also by the action of hydrogen sulphide on copper allyldiguanidine suspended in water. It forms a slightly crystalline, very hygroscopic mass, is strongly alkaline in character, displacing ammonia from its salts and absorbing carbonic anhydride from the air. When heated with potash and chloroform, it yields allylcarbamine ($C_3H_5{\cdot}NC$).

In chemical characteristics, the above copper compound somewhat resembles the alkaline earthy metals, the allyldiguanidine, the alkali metals and especially sodium. L. T. T.

Isonitroso-compounds. By E. Beckmann (*Ber.*, **20**, 2580—2585; compare Abstr., 1887, 826).—The intramolecular change which takes place when diphenylketoxime is treated with phosphorus pentachloride or with sulphuric acid, is also produced by hydrochloric acid, acetic chloride, acetic anhydride, and acetic acid.

When a cooled solution of diphenylketoxime in 10 parts of glacial acetic acid containing acetic anhydride is saturated with hydrogen chloride, and then heated at 100°, the oxime is completely converted into benzanilide; this is precipitated by sodium carbonate, and recrystallised from alcohol. Methylphenylketoxime when similarly treated yields acetanilide, which separates as hydrochloride on cooling the solution; the reaction takes place in the cold, but requires some days.

Methylpropylketoxime is converted by hydrochloric acid into the compound $NHPr{\cdot}CMeO,HCl$, and not into the compound $NHMe{\cdot}CPrO$. When diphenylketoxime is heated with acetic anhydride in presence of hydroxylamine hydrochloride at 150°, acetanilide and benzoic acid are formed. Methylphenylketoxime when heated with 10 parts of acetic anhydride for six hours at 100°, yields the compound $CMePh\colon N{\cdot}OAc$ (Rattner, *Ber.*, **20**, 506). This crystallises from light petroleum in forked needles melting at 55°.

Glacial acetic acid at 180° acts on diphenylketoxime with formation of benzanilide, acetanilide, and benzoic acid. Methylphenylketoxime is converted by hot glacial acetic acid into oily products; acetanilide is not formed. N. H. M.

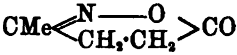
Oxidation by Means of Hydrogen Peroxide. By C. Wurster (*Ber.*, **20**, 2631—2633).—The author showed previously (*Centr. für Physiol.*, 1887, 33) that organic acids are quickly oxidised by hydrogen peroxide to carbonic anhydride; the higher fatty acids and oils, cane- and grape-sugar, are rather stable towards hydrogen peroxide, whilst boiled starch is converted first into erythrodextrin and then into sugar.

Hydrogen peroxide (6 mols.) reacts with hydroxylamine sulphate at 40° with formation of sulphuric acid, nitric acid (2 mols.), and water (12 mols.). Hydroxylamine hydrochloride is similarly converted into hydrochloric and nitric acids and water. The yield is quantitative.

When an aqueous solution of phenol is treated with a hydroxylamine salt and hydrogen peroxide, nitrosophenol is formed.

Phenylhydrazine is converted by hydrogen peroxide into benzene and diazobenzeneimide. The production of benzene makes it probable that free diazobenzene is first formed in the oxidation of the hydrazine. N. H. M.

Isonitrosovaleric Acid and γ-Valeroximidolactone. By P. RISCHBIETH (*Ber.*, **20**, 2669—2673).—Isonitrosovaleric acid (Abstr., 1883, 1129) can readily be obtained by dissolving hydroxylamine hydrochloride (50 grams) and levulinic acid (83 grams) in a small quantity of water and adding a concentrated aqueous solution of sodium carbonate (38 grams); a separation of the acid immediately occurs, and this is purified by recrystallisation from water. The yield amounts to 90 per cent. of that theoretically possible. When treated with hydrogen chloride, the acid melts and absorbs the gas, and on warming the product, a sudden reaction occurs with the evolution of nitrogen, and production of a black residue. On oxidation with dilute nitric acid, a large volume of gas is evolved, and acetic and succinic acids are formed; the residue is, moreover, found to be free from nitrogen. If the acid (6 grams) is heated with sulphuric acid (10 grams) in a vacuum at 150°, succinic acid sublimes, and nitrogen is evolved; when, however, a much larger proportion of sulphuric acid (36 grams) is employed, and the heating is continued for 6 to 12 hours at 100° at the ordinary pressure, the elements of a molecule of water are withdrawn from the molecule of isonitrosovaleric acid, and the "inner anhydride," γ-valeroximidolactone, together with succinic acid, results.

γ-Valeroximidolactone,  $\mathrm{CMe}\!<\!\begin{matrix}\mathrm{N}\text{——}\mathrm{O}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!>\!\mathrm{CO}$, crystallises from ether and water in long, white prisms; it melts at 69—70° when slowly heated, and at a somewhat higher temperature when the heating is rapid, and boils at 232° without decomposition. When heated with aqueous alkalis, it yields the corresponding salts of isonitrosovaleric acid, but dilute sulphuric acid, hydrogen chloride, fuming hydrochloric acid, and ammonia are without action on it at 100°. On distillation with nitric acid (sp. gr. = 1·4), a distillate is obtained which contains in addition to unaltered lactone at least two distinct crystalline compounds; these have not yet been further examined. W. P. W.

New Source of Capric Acid. By A. BUISINE and P. BUISINE (*Compt. rend.*, **105**, 614—617).—Capric acid does not exist as such in suint, but an aqueous solution of suint undergoes fermentation under the influence of microbes, and the quantity of fatty acids and especially of capric acid is greatly increased, the proportion of the latter rising to 5 per cent.

The capric acid is separated by distillation, saponification, and subsequent fractionation, and is finally crystallised from boiling water. It forms a crystalline, buttery mass, with an odour of rancid butter, melts at 31°, is soluble in alcohol and ether, and is slightly soluble in boiling water, from which it crystallises in white needles. The barium salt is soluble in alcohol. C. H. B.

Linoleic Acid. By L. M. NORTON and H. A. RICHARDSON (*Ber.*, **20**, 2735—2736).—When endeavouring to dry linoleic acid at 100° in a current of hydrogen, the authors found that a continued loss of weight occurred even after 28 hours, although no change in composition took place. Linoleic acid can be distilled without any appearance of decomposition at 290° under 89 mm. pressure, and a colourless product is obtained amounting to about three-fourths of the acid taken. This consists of an acid, $C_{20}H_{36}O_3$, which cannot again be distilled in a vacuum without decomposition; its sp. gr. is 0·9108 at 15°, and its vapour-density = 153.

Under similar conditions, ricinoleic acid yields an acid agreeing in composition with that just described. W. P. W.

Butanedicarboxylic Acid. By R. Otto and A. Rössing (*Ber.*, **20**, 2736—2747).—By the reduction of dimethylmaleïc acids, two butanedicarboxylic acids are obtained, the one, melting at 193—194°, which has been shown to be symmetrical dimethylsuccinic acid, the other, ethylmethylmalonic acid, melting at 118—120°. In this paper, the anhydrides of these acids are more particularly studied. The former on dry distillation yields an anhydride melting at 87°, previously described by Bischoff and Rach; but this substance on rehydration and crystallisation from the aqueous solution yields not only the original or symmetrical dimethylsuccinic acid, but also the above-mentioned isomeric ethylmethylmalonic acid. On the other hand, the symmetrical dimethylsuccinic acid, when treated with excess of acetic chloride, yields an anhydride isomeric with the above, which crystallises in rhombic tables melting at 38°; this on rehydration yields the original acid only.

Again the butanedicarboxylic or ethylmethylmalonic acid, melting at 121°, remains unaltered on dry distillation, but when treated with acetic chloride it yields an anhydride of the same melting point, 86—87°, and crystalline form as the former of the anhydrides mentioned above, but which, however, differs from it in yielding on rehydration the original acid only. V. H. V.

Distillation of Citric Acid with Glycerol. By P. de Clermont and P. Chautard (*Compt. rend.*, **105**, 520—523).—500 grams of crystallised citric acid mixed with 750 grams of ordinary glycerol of 28° are distilled in a glass retort of 3 litres capacity, and the product redistilled. The first fraction consists of about 250 grams of water containing a small quantity of acraldehyde, &c.; some crystals also separate in the colder part of the apparatus. The mass then swells up, and the temperature must be reduced, but it is afterwards gradually raised until the distillation is complete. The distillate during this second stage consists of 650 to 700 grams of liquid. The total products of the decomposition are 950 grams of liquid, 30 grams of a bulky, carbonaceous residue, carbonic oxide and carbonic anhydride, and vapours of acetone and acraldehyde. In addition to water containing small quantities of acraldehyde, the only products in the distillate are unaltered glycerol and pyruvine or the pyruvic ether of glycide, $MeCO\cdot COO\cdot CH_2\cdot CH<\genfrac{}{}{0pt}{}{CH_2}{-O-}>$, which is also obtained by the distillation of glycerol with tartaric acid or glyceric acid. Probably the pyruvine is a product of the reaction between glycerol and glyceric acid, the latter being formed as an intermediate product.

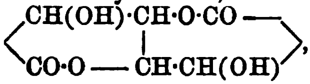
The pyruvine thus obtained crystallises in large, prismatic needles, or tables, which melt at 82° and boil at 241° under a pressure of 764 mm.
C. H. B.

Double Lactone of Metasaccharic Acid. By H. KILIANI (*Ber.*, **20**, 2710—2716).—The oxidation product of the lactone of arabinose-carboxylic acid (Abstr., 1887, 465) dissolves readily in aqueous ammonia, and from the solution the *diamide* of *metasaccharic acid*, $C_6H_{12}O_6N_2$, separates as a white powder, consisting of microscopic, tabular, monoclinic crystals, which become yellow at 170° and melt at 189—190° with complete decomposition. The compound has a neutral reaction, and when heated at 100° with potassium hydroxide yields the potassium salt of metasaccharic acid as a colourless syrup; this becomes crystalline on stirring, and in aqueous solution does not reduce Fehling's solution.

On treatment with a cold solution of phenylhydrazine hydrochloride (1 part) and sodium acetate (1·5 part), in water (10 parts), the oxidation product yields the *monophenylhydrazide* of the *lactone* of *metasaccharic acid*, $C_{12}H_{14}O_6N_2$; this crystallises in colourless, microscopic scales with $\frac{1}{2}$ mol. H_2O, dissolves readily in hot water and alcohol, and when rapidly heated becomes yellow at 185°, and melts at 190—192° with decomposition. If the mixture with phenylhydrazine (which, to obtain the preceding compound is allowed to remain for 20 minutes for the crystallisation to take place) is at once poured into boiling water, the *diphenylhydrazide* of *metasaccharic acid*, $C_{18}H_{22}O_6N_4$, separates after 10 to 15 minutes in yellowish-white, microscopic scales, which become yellow at 210°, melt at 212—213° with decomposition, and are very sparingly soluble in boiling water and alcohol. The solution in concentrated sulphuric acid is coloured red or bluish-violet by ferric chloride.

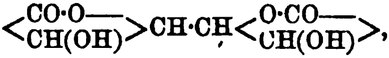
When the oxidation product (12 grams) is dissolved in water (300 grams), treated with 3 per cent. sodium amalgam (200 grams), and dilute sulphuric acid added gradually so that the solution never becomes alkaline, allowed to remain five days with a further 200 grams of sodium amalgam, then treated with sulphuric acid and alcohol to free the product from sodium sulphate, and the mother-liquor evaporated, a syrup is obtained which still reduces alkaline copper solution, and from which mannite (2 grams) crystallises on standing over sulphuric acid. The strongly acid mother-liquor seems to consist of the lactone of a bibasic acid (? metasaccharic acid), a strongly acid syrup having similar properties being also obtained by continued heating of the oxidation product with water, or by repeated evaporation of its aqueous solution.

The oxidation product of the lactone of arabinose-carboxylic acid dissolves in 18, not 8, parts of cold water (compare *loc. cit.*), and readily reduces alkaline copper solution. The aqueous solutions of its potassium and sodium salts, even in the absence of free alkali, become coloured intensely red on heating, or when allowed to evaporate spontaneously (*Ber.*, **20**, 343). The author, however, concludes, from the preceding experiments, that the oxidation product is not the lactone of a ketonaldehydic acid, but is a double lactone of metasaccharic acid,



$$\left\langle\begin{matrix}\mathrm{CH(OH)\cdot CH\cdot O\cdot CO}\text{——} \\ | \\ \mathrm{CO\cdot O}\text{——}\mathrm{CH\cdot CH(OH)}\end{matrix}\right\rangle$$

, or



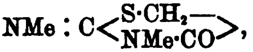
$$<^{\mathrm{CO\cdot O}\text{——}}_{\mathrm{CH(OH)}}>\mathrm{CH\cdot CH}<^{\mathrm{O\cdot CO}\text{——}}_{\mathrm{CH(OH)}}>,$$

which, on account of its peculiar constitution is very labile, and on treatment with alkalis even at the ordinary temperature undergoes molecular change, or perhaps reduction to an aldehyde-compound yielding mannite by the action of nascent hydrogen. W. P. W.

Thiohydantoïn. By R. ANDREASCH (*Monatsh.*, 8, 407—424).—Loven has recently shown (Abstr., 1885, 241) that a methylene-group situated between a carbonyl-group and a sulphur-atom possesses similar properties to the methylene-group in ethyl malonate and acetoacetate. With the object of ascertaining whether this is the case in hydantoïn, the author has prepared the disilver-derivative, and from that the dimethyl-compound.

Disilverthiohydantoïn, $Ag_2C_3N_2H_2SO$, was obtained by adding a warm aqueous solution of thiohydantoïn to ammoniacal silver nitrate. It forms a white, granular substance, sparingly soluble in nitric acid, insoluble in ammonia. It blackens when exposed to light. When treated with methyl iodide, the silver compound yields *β-dimethylthiohydantoïn*, $\mathrm{NH : C}<^{\mathrm{S\cdot CMe_2}}_{\mathrm{NH\cdot CO}}>$. This substance is easily soluble in water, sparingly in cold alcohol, crystallises in hexagonal scales, melts at 114°, and decomposes at a slightly higher temperature. When oxidised in hydrochloric solution by barium chlorate, carbonic anhydride and mercaptan are evolved, and the residue is found to contain carbamide, and a mixture of barium salts which cannot be separated, but one of which seems to be barium methylsulphonate. When heated with barium hydroxide, the hydantoïn yields cyanamide and some sulphur compounds which could not be isolated.

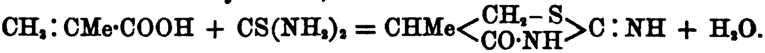
With the aim of determining the constitution of the above compound, the author attempted to prepare the two isomeric dimethylhydantoïns in other ways. *α-Dimethylthiohydantoïn*,



$$\mathrm{NMe : C}<^{\mathrm{S\cdot CH_2}\text{—}}_{\mathrm{NMe\cdot CO}}>,$$

may be prepared by heating together dimethylthiocarbamide and chloracetic acid in aqueous solution. It is easily soluble in water, alcohol, ether, and carbon bisulphide, crystallises in long, thin, colourless prisms, melts at 71°, and boils at a rather higher temperature. It volatilises slowly at ordinary temperatures. It has an odour somewhat resembling that of nicotine. When heated with aqueous alkalis, it yields thioglycollic acid. The *isonitroso*-derivative, $C_5H_7N_3SO_2$, yields yellowish scales melting at 220°. *Imidocarbaminethioisobutyric anhydride*, $C_5N_2H_8SO$, was prepared by heating together thiocarbamide and α-bromisobutyric acid. It crystallises in plates, is easily soluble in alcohol and boiling water, sparingly in cold water, and melts at 242°. When oxidised with nitric acid, this substance yields carbamide and *sulphoisobutyric acid*, $SO_3H{\cdot}C_3H_6{\cdot}COOH$, which forms a *barium* salt, $BaC_4H_6SO_5 + 4H_2O$, crystallising in needles, easily soluble in water, insoluble in alcohol. The *sodium salt*, $Na_2C_4H_6SO_5 + \frac{1}{2}H_2O$, forms glistening needles easily soluble in water, insoluble in alcohol. The same sulpho-acid is obtained by the action of chlorosulphonic acid on isobutyric acid. The action of ammonium sulphite on α-bromisobutyric acid produces, however, an isomeric sulpho-acid, yielding an easily soluble *barium salt*, $BaC_4H_6SO_5 + 2H_2O$, crystallising in needles.

It is thus clear that this imido-anhydride is not identical with the β-dimethylthiohydantoïn, as the author had anticipated. As it was possible that in the formation of the imido-anhydride a transformation from the iso- to the normal butyric series had occurred, the author prepared *imidocarbaminethiobutyric anhydride*, $NH : C{<}\genfrac{}{}{0pt}{}{S{\cdot}CHEt}{NH{\cdot}CO}{>}$, by the action of α-bromobutyric acid on thiocarbamide. This crystallises in short, thick needles, easily soluble in boiling water, and melts at 200°. It is not identical with the compound obtained from isobutyric acid. The constitution of the latter is therefore still doubtful, but its formation may perhaps be due to the action of thiocarbamide on the methacrylic acid formed by the elimination of hydrogen bromide from the bromisobutyric acid,



$$CH_2 : CMe{\cdot}COOH + CS(NH_2)_2 = CHMe{<}\genfrac{}{}{0pt}{}{CH_2-S}{CO{\cdot}NH}{>}C : NH + H_2O.$$

The consitution of the β-compound would then be correctly expressed by the formula given above.

Thiohydantoïn when treated with benzaldehyde yields *amidinethiocinnamic* (*benzylidenethiohydantoïc*) *acid*, $NH : C(NH_2)(COOH) : CHPh$; this forms white, microscopic needles, insoluble in water, soluble in alcohol. Similar acids seem to be produced with other aldehydes.

Several salts of thiohydantoïn are described. The *sulphate*, $(C_3H_4N_2SO)_2,H_2SO_4$, forms plates soluble in water; the *nitrate*, flat needles or prisms; the *oxalate*, $C_3H_4N_2SO,C_2H_2O_4 + H_2O$, prisms; the *picrate* yellow, microscopic needles.

Thiohydantoïn is best prepared as follows: 50 grams of thiocarbamide is dissolved in ½ litre water, and 62 grams of chloracetic acid dissolved in 50 c.c. of water added. The whole is heated at 80—90° until reaction has ceased, and when cold it is gradually neutralised with soda, care being taken never to let the solution become alkaline.

L. T. T.

Orthothioxen and Orthothiophendicarboxylic Acid. By W. GRÜNEWALD (*Ber.*, 20, 2585—2587).—Orthothioxen (Paal, Abstr., 1887, 1101) is prepared by distilling an intimate mixture of 10 grams of β-methyllevulinic acid and 17 grams of phosphorus trisulphide in a capacious retort. 250 grams of methyllevulinic acid yielded 150 grams of pure product. It is a colourless, strongly refractive oil, having an odour of petroleum; it boils at 136—137° (corr.). Sp. gr. at 21° = 0·9938. When treated with 1 per cent. solution of potassium permanganate, a monocarboxylic acid only is formed; this melts at 134·5°.

Orthothiophendicarboxylic acid, $C_4SH_2(COOH)_2$, is obtained by the action of 1 per cent. permanganate solution on the monocarboxylic acid; the product is steam-distilled to remove unchanged monocarboxylic acid. It crystallises in long needles which do not melt at 260°, but decompose at a higher temperature. When heated with resorcinol at 200°, a product is obtained which dissolves in strong aqueous alkali with dark-red coloration; the colour changes to yellow on diluting with water; the solution then shows a yellowish-green fluorescence. The *silver salt* forms white flakes insoluble in water; the *barium salt* separates in colourless crystals, readily soluble in hot water. The dimethyl salt crystallises from alcohol in colourless plates melting at 59·5°. N. H. M.

Action of Carbonic Anhydride on Aromatic Amines. By A. DITTE (*Compt. rend.*, **105**, 612—614).—When an aniline salt is mixed with an aqueous solution of a normal or hydrogen carbonate, carbonic anhydride is given off, and aniline separates in the free state, no aniline carbonate being formed. Carbonic anhydride is not soluble in aniline, and does not combine with it under ordinary pressure even at —8°, the temperature at which aniline solidifies.

If, however, dry carbonic anhydride and aniline are compressed in a Cailletet's apparatus, the aniline dissolves the carbonic anhydride, increasing to about twice its original volume, and a limpid layer of the liquefied gas swims on the surface of the solution and volatilises at 15° under a pressure of 40 atmos. If the compressed liquid is cooled to 8—10°, it crystallises in transparent, white needles, and when the aniline and carbonic anhydride are in equal molecular proportions, solidification is complete. When the carbonic anhydride is in excess, it forms a layer above the crystals. When aniline is in excess, it does not at once dissolve the carbonic anhydride, and the two liquids form distinct layers, but on gentle agitation the carbonic anhydride is dissolved, and crystallisation takes place at 8°. It is evident that carbonic anhydride and aniline combine in equal molecular proportions to form a compound which crystallises at 8°, and is liquid or remains in superfusion at 10°, and decomposes when the pressure is released. The tension of dissociation at different temperatures is as follows:—

Temperature	0°	2°	5°	7°
Pressure in atmos.	6	9	17	28

Orthotoluidine behaves in a precisely similar manner, and the compound crystallises in brilliant, white needles. The behaviour of metaxylidene is similar in that the two liquids mix, but no crystals form even at —12°.

Pyridine and its homologues show no tendency to combine with carbonic anhydride; the two liquids do not mix. C. H. B.

Benzylidene Compounds. By L. KOHLER (*Annalen*, **241**, 358—362).—An alcoholic solution of benzylideneparatoluidine is converted into benzylparatoluidine by the action of sodium amalgam. The base distils at 312—313°, and solidifies in the course of several weeks. It is freely soluble in alcohol and ether. The hydrochloride is soluble in alcohol and in hot benzene, and the sulphate is soluble in water. The nitroso-compound melts at 53°.

Benzyl-β-naphthylamine crystallises in prisms, and melts at 68°. The nitroso-derivative forms yellow needles, soluble in alcohol, ether, benzene, and light petroleum. It melts at 111—112°.

Benzylamidodimethylaniline, prepared from the condensation-product of benzaldehyde and amidodimethylaniline, melts at 48°, and distils without decomposition. The *nitrosamine* is deposited from alcohol in yellow needles. It melts at 127—128° with decomposition.

W. C. W.

Reduction Products of Benzylidene Compounds. By O. Fischer (*Annalen*, **241**, 328—331).—The author has previously pointed out (Abstr., 1886, 546) that 3 per cent. sodium amalgam reduces a solution of hydrobenzamide in absolute alcohol to dibenzylamine and monobenzylamine; ammonia and toluene are always liberated during the reaction. Under similar treatment, benzylideneaniline is converted into benzylaniline.

The salt which is deposited when nitrosobenzylaniline is treated with alcoholic hydrogen chloride is a mixture of benzylaniline hydrochloride and benzylidene aniline. W. C. W.

Hydroxybenzylidene Compounds. By O. Emmerich (*Annalen*, **241**, 343—358).—*Orthohydroxybenzylaniline*, $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHPh$, is obtained by the action of sodium amalgam on a solution of hydroxybenzylideneaniline in absolute alcohol. It melts at 106°, and is soluble in alcohol and ether. The sulphate and hydrochloride are freely soluble in water. The platinochloride forms reddish-yellow needles, melting at 184° with decomposition. A tetranitro-derivative, $C_{13}H_9NO(NO_2)_4$, is formed when the base is treated with a mixture of sulphuric and nitric acids. It melts at 66° with decomposition, and is soluble in alcohol, acetic acid, and light petroleum.

Orthohydroxybenzylparatoluidine, $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4Me$, obtained by the reduction of the hydroxybenzylideneparatoluidine, crystallises in white plates and needles, and melts at 116°. It is soluble in alcohol and ether. The sulphate and hydrochloride dissolve freely in water. The platinochloride crystallises in needles. The tetranitro-derivative forms yellow needles, soluble in alcohol, benzene, and acetic acid. It melts at 168°. By the action of methyl iodide, the base is converted into *orthomethoxybenzylparatoluidine*,

$$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4Me,$$

a crystalline compound melting at 110°, and soluble in alcohol, ether, and benzene.

Orthodihydroxydibenzylamine is prepared by the action of sodium amalgam on an alcoholic solution of hydrosalicylamide. It crystallises in needles, melts at 170°, and dissolves freely in ether, alcohol, benzene, and light petroleum. The sulphate, nitrate, and hydrochloride are soluble in water. The platinochloride crystallises in needles, and is soluble in water.

The condensation compound of salicylaldehyde and β-naphthylamine yields on reduction *orthohydroxybenzyl-β-naphthylamine*,

$$OH·C_6H_4·CH_2·NH·C_{10}H_7,$$

a crystalline substance melting at 147°. It is soluble in alcohol, ether, benzene, and light petroleum. The alcoholic solution exhibits a reddish-violet fluorescence. The sulphate is liquid, and the platinochloride crystallises with difficulty.

Orthohydroxybenzyl-β-naphthylnitrosamine melts at 165° with decomposition. On exposure to the air, the compound decomposes spontaneously at the ordinary temperature. It is soluble in alcohol and ether. *Orthomethoxybenzyl-β-naphthylamine* crystallises in needles, melts at 92°, and dissolves freely in alcohol and ether.

Parahydroxybenzylaniline, prepared from parahydroxybenzylideneaniline, is soluble in alcohol and ether. It melts at 208°, and forms a crystalline platinochloride.

Parahydroxybenzyltoluidine melts at 186°. *Parahydroxybenzyl-β-naphthylamine* melts at 117°. The sulphate is soluble in alcohol, but almost insoluble in water. The *nitrosamine* melts at 142°, and dissolves in alcohol and ether. It is unstable. W. C. W.

Anisylamines. By O. J. STEINHART (*Annalen*, **241**, 332—343).—A solution of anishydramide in absolute alcohol is converted into a mixture of mono- and di-anisylamine by the action of sodium amalgam at the ordinary temperature. *Dianisylamine*, $NH(CH_2·C_6H_4·OMe)_2$, forms white, needle-shaped crystals soluble in alcohol and ether. It melts at 34°, and decomposes on distillation. The *hydrochloride* is soluble in alcohol, and crystallises in flat prisms. It melts at 243°. The platinochloride is crystalline but unstable. The *nitroso*-derivative, $(OMe·C_6H_4·CH_2)_2N·NO$, crystallises in needles, and melts at 80°. *Anisylamine* is a colourless liquid boiling at 220—223°. It is miscible with alcohol, ether, and water, and it absorbs carbonic anhydride from the air. It can be separated from dianisylamine by its volatility in a current of steam. The hydrochloride forms white plates which are freely soluble in water, and melt at 230°. The platinochloride crystallises in pale-yellow, glistening needles. It melts at 210°.

Anisylaniline, $MeO·C_6H_4·CH_2·NHPh$, prepared from anishydranilide, crystallises in prisms, and dissolves freely in the usual solvents. It melts at 64·5°, and forms a crystalline hydrochloride, sulphate, and platinochloride. The *nitroso*-derivative melts at 104°. It crystallises in prisms, and is soluble in alcohol.

Anishydroparatoluide, $OMe·C_6H_4·CH\colon NC_6H_4Me$, forms white needles, and melts at 92°. *Anisylparatoluidine*, $OMe·C_6H_4·CH_2·NH_2·C_6H_4Me$, forms white prisms, melting at 68°. It is soluble in all the usual solvents with the exception of water. The hydrochloride and platinochloride are crystalline, but the salts have a tendency to decompose when their solutions are evaporated. The *nitrosamine* melts at 108°.

Anisaldehyde and orthotoluidine condense, forming anishydrorthotoluide, which yields orthotoluylanisylamine on reduction. The base melts at 55°. The nitrosamine is an oily liquid.

Anisylidenenaphthylamine(β), $OMe\cdot C_6H_4\cdot CH\colon NC_{10}H_7$, crystallises in plates, and melts at 98°. *Anisyl-β-naphthylamine* is soluble in alcohol, benzene, and in light petroleum. It melts at 101°. The salts are sparingly soluble in water, and are rather unstable. The nitrosamine melts at 133°, and crystallises in plates. *Anisylidenedimethylparaphenylenediamine* forms greenish-yellow needles. It melts at 148°, and yields on reduction *anisyldimethylparaphenylenediamine*, $OMe\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot NMe_2$. This base crystallises in plates, and melts at 104°. The alcoholic solution decomposes on exposure to the air, and the nitroso-compound is unstable. W. C. W.

Salts of Picramic Acid. By A. SMOLKA (*Monatsh.*, 8, 391—398). —The salts of this acid having been but little studied, the author has prepared and examined a number of them. In some cases they were obtained by the direct action of picramic acid on the metallic carbonate, in others by double decomposition. The following table shows the results obtained :—

Formula of salt.	Description.	Ratio of solubility in water.		Temperature of decomposition.
		I. Boiling.	II. Cold.	
$NaC_6H_4N_3O_5 + H_2O$	Dark red crystals	1:48·6 at 15·5°	freely	about 150°
$Mg(C_6H_4N_3O_5)_2 + 3H_2O$.	Dark reddish-brown scales	1:17·9 „ 17·0	freely	140
$Zn(C_6H_4N_3O_5)_2 + H_2O$ ..	Yellow, microscopic needles	1:5890 „ 23·0	1:1842	140–150°
$Cd(C_6H_4N_3O_5)_2 + H_2O$ ..	Greenish-yellow needles	1:1215 „ 23·0	1:318	140°
$Hg_2(C_6H_4N_3O_5)_2$	Scarlet, microscopic crystals	1:21010 „ 17·5	1:12481	120
$Hg(C_6H_4N_3O_5)_2 + H_2O$.	Dull yellow, microscopic needles	1:3172 „ 18·0	1:1151	140–145°
$Pb(C_6H_4N_3O_5)_2$	Small, reddish-brown needles	1:2632 „ 20·5	1:1494	140–150
$Mn(C_6H_4N_3O_5)_2 + 2H_2O$.	Dark steel-green needles	1:97·5 „ 19·0	freely	150°
$Co(C_6H_4N_3O_5)_2$	Greenish-yellow, amorphous powder	insoluble	1:3292	140
$Ni(C_6H_4N_3O_5)_2$	Dark olive-green, amorphous powder	insoluble	1:3532	140–145°

If the salt is heated slowly, the decomposition takes place quietly, but if rapidly, explosions occur, especially with the sodium and lead salts. The aqueous solutions vary in colour from pale orange to dark blood-red. L. T. T.

Chlorine and Bromine-derivatives of Citraconanil. By T. MORAWSKI and J. KLAUDY (*Monatsh.*, 8, 399—406).—*Citraconparachloranil*, $C_5H_4O_2 : N{\cdot}C_6H_4Cl$, is formed (together with chloranilines) when a stream of chlorine is passed into water in which finely-divided citraconanil is suspended. It crystallises in white, glistening needles, soluble in alcohol and melting at 114·5°. With care it may be sublimed in long, glass-like needles. When heated with ammonia, it yields parachloraniline and citraconic acid, showing the correctness of the above formula.

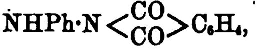
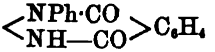
When bromine acts on citraconil, *bromocitraconparabromanil*, $C_5H_3BrO_2 : N{\cdot}C_6H_4Br$, is formed. This crystallises in white, shining needles, soluble in alcohol and melting at 178°. It can be sublimed, but decomposes if heated rapidly. When heated with ammonia, parabromaniline is formed, together with hydrogen bromide, much resinous matter, and an acid of the formula $C_7H_9BrO_4$. This acid yields a *silver* salt, $Ag_2C_7H_7BrO_4$, crystallising in prisms, and a lead salt, $PbC_7H_7BrO_4$, forming microscopic crystals. It appears, therefore, that the original bromo-derivative contained one bromine-atom in the citraconic nucleus, and that when heated with ammonia this nucleus is converted into a higher brominated homologue of the citraconic series, together with other byo-products.

When only enough bromine is employed for the formation of *citraconparabromanil*, white, crystalline needles melting at about 118° were obtained, but this compound has not yet been obtained in a pure state. L. T. T.

Action of Phenylhydrazine on Ethyl Chloracetoacetate. By G. BENDER (*Ber.*, **20**, 2747—2752).—Ethyl chloracetoacetate reacts with phenylhydrazine in ethereal solution to form a compound, $C_{12}H_{14}N_2O_2$; it is probable that a hydrazine-derivative,

$$NHPh{\cdot}N : CMe{\cdot}CHCl{\cdot}COOEt,$$

is at first formed, which is subsequently converted into a compound, $NPh : N{\cdot}CHMe{\cdot}CHCl{\cdot}COOEt$, and finally by abstraction of the elements of hydrogen chloride into $NPh : N{\cdot}CMe : CH{\cdot}COOEt$, or ethylic β-phenylazocrotonate. This substance crystallises in long, red needles, melting at 50·5°, very soluble in alcohol; on saponification, it yields a potassium salt, $NPh : N{\cdot}CMe : CH{\cdot}COOK$, which forms reddish-yellow scales, very soluble in water, insoluble in alcohol. The salt on acidification yields the corresponding anhydride as a brownish-yellow powder, whose purification presents considerable difficulty. Ethylic β-phenylazocrotonate when reduced yields phenylmethylpyrazolone and its first oxidation product or its bis-derivative, together with a substance not further examined. The bis-derivative yields with bromine a compound, $C_{20}H_{21}N_4O_4Br$, which crystallises in colourless needles, melting at 217° with decomposition. α-Naphthylamine with ethylic chloracetoacetate yields a compound, $C_{16}H_{16}NO_2Cl$; this crystallises in colourless prisms, melting at 75°; its formation is due to a change analogous to the first of the reactions given above in the case of phenylhydrazine. V. H. V.

Isomeric Phthalophenylhydrazines. By G. Pellizari (*Gazzetta*, 17, 278—285).—The author has previously described two isomeric phthalyl-derivatives of phenylhydrazine obtained by the action of this base on phthalimide and phthalic anhydride respectively (Abstr., 1886, 125). To the former, melting at 179°, the constitution  $\mathrm{NHPh{\cdot}N}\genfrac{<}{>}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}\mathrm{C_6H_4}$, to the latter, melting at 210°, the constitution  $\genfrac{<}{>}{0pt}{}{\mathrm{NPh{\cdot}CO}}{\mathrm{NH{—}CO}}\mathrm{C_6H_4}$ was assigned. If these formulæ are correct, a methyl-derivative of the former, or anilophthalimide, on separation of the phthalyl grouping, should yield a symmetrical methylphenylhydrazine, $NPhMe{\cdot}NH_2$, that of the latter, or phthalophenylhydrazine, the symmetrical derivative, $NHPh{\cdot}NHMe$. Phthalophenylhydrazine, heated with methyl iodide and alcohol, yields a methyl-derivative, crystallising in long, yellowish-white prisms, which melt at 125° without decomposition; this is decomposed by concentrated hydrochloric acid, yielding methylphenylhydrazine, $NHPh{\cdot}NHMe$. The constitution of the isomeride has previously been proved by Hötte, but in answer to his criticisms (Abstr., 1887, 770) it is shown that phthalic anhydride and phenylhydrazine, reacting in molecular proportions, give either anilophthalimide or phthalophenylhydrazine, according to the temperature; at ordinary temperatures, phenylhydrazine-phthalic acid is at first formed, which on subsequent heating yields anilophthalimide; if, however, the reaction proceeds at 163°, the melting point of the acid, at which temperature it is unstable, phthalophenylhydrazine is formed in the greater proportion.

V. H. V.

Dyes from Aniline Chromates. By S. Grawitz (*Compt. rend.*, **105**, 576—577).—A question of priority and patent right.

Azophenine. By O. N. Witt (*Ber.*, **20**, 2659—2660).—A reply to Fischer and Hepp (Abstr., 1887, 1105), in which the author points out that the constitutional formula proposed by them is inadmissible, since azophenine does not form an acetyl-derivative when heated with acetic anhydride, and yields a considerable quantity of aniline on treatment with tin and hydrochloric acid. On these grounds, the author adheres to his published views on the constitution of azophenine (Abstr., 1887, 821).

W. P. W.

Substituted Safranines. By P. Barbier and L. Vignon (*Compt. rend.*, **105**, 670—672).—Paranitrosodimethylaniline has no action on aniline at the ordinary temperature in presence of water, glacial acetic acid, or an excess of aniline, but at 80° there is an extremely violent reaction.

If equal molecular proportions of aniline and paranitrosodimethylaniline are dissolved in eight times their weight of ethyl alcohol of 92°, and heated on a water-bath, a reaction takes place at 80°, with considerable development of heat, and is complete in about three hours. When the liquid is cooled, a solid separates, which is washed with dilute hydrochloric acid, and then crystallised from boiling toluene. *Tetramethyldiamido-azobenzene* is thus obtained in brilliant, brown, crystalline plates, which melt imperfectly at 218—220° without volatilisation, and when reduced with zinc and sulphuric acid, yield dimethylparaphenylenediamine in almost theoretical quantity. It is almost insoluble in water, and only slightly soluble in dilute acids, but dissolves in concentrated acids forming deep red solutions.

The alcoholic liquid separated from the tetramethyldiamido-azobenzene has a deep, violet-red colour, and when evaporated leaves a viscid residue, which dissolves almost completely in water. When this solution is mixed with sodium carbonate, a precipitate is formed, and if the filtrate is mixed with sodium chloride, dimethylphenosafranine separates, and is purified by repeating the treatment with sodium carbonate and chloride.

The equation representing the reaction is—

$$2NH_2Ph + 3C_6H_4NO{\cdot}NMe_2,HCl = C_{16}H_{20}N_4 + C_{20}H_{19}N_4Cl + 3H_2O + 2HCl.$$

C. H. B.

Action of Acid Amides on Bromacetophenones. By M. Lewy (*Ber.*, **20**, 2576—2580).—When bromacetophenone is heated with acetamide (2 parts) at 120—130°, for one hour, a *base*, $C_{10}H_9NO$, is obtained. This forms long, colourless needles, readily soluble in alcohol and ether; it melts at 45°, and boils at 241—242°; it has slightly basic properties. The hydrochloride, $C_{10}H_9NO,HCl$, crystallises in small needles; when treated with an excess of hydrogen chloride, it yields a heavy, fuming oil, possibly an acid salt. The *platinochloride*, $(C_{10}N_9NO)_2,H_2PtCl_6 + 2H_2O$, separates in dense, yellow flakes, consisting of orange-coloured needles, which melt at 130—140 with decomposition. The *sulphate* forms white, lustrous plates, which decompose in contact with water. The *picrate* crystallises in lemon-coloured needles, melting at 133—134°.

The *formamide base*, C_9H_7NO, prepared by heating bromacetophenone with formamide, is a thick, colourless oil, which becomes yellow when exposed to air; it solidifies when cooled with a freezing mixture, melts at 6°, and boils at 220—222°. The *hydrochloride* melts at 80°. The *platinochloride* (with 2 mols. H_2O) crystallises in slender, yellow needles. The *benzamide base*, $C_{15}H_{11}NO$, is prepared by heating bromacetophenone and benzamide at 140—150°; the product is extracted several times with boiling water, and the residue fractionally distilled. It crystallises from alcohol in large, colourless plates, readily soluble in the usual solvents, melts at 102—103°, and boils at 338—340°. The hydrochloride crystallises in slender, matted needles; it is slowly decomposed by boiling water. N. H. M.

Isonitroso-compounds: Isobenzaldoxime. By E. Beckmann (*Ber.*, **20**, 2766—2768).—When benzaldoxime is mixed with sulphuric acid in presence of ice, a solid, white substance separates out under certain conditions; sometimes an oil is obtained. The former, probably a polymeride of benzaldoxime, crystallises in glistening needles, melting at 128—130°; it is distinguishable from benzamide by its crystalline form. The oil is benzaldehyde, produced by the re-formation of the oxime and its subsequent decomposition by the acid present. V. H. V.

Condensation of Cinnamic Acid with Gallic Acid. By E. JACOBSEN and P. JULIUS (*Ber.*, **20**, 2588—2589).—*Styrogallol*, $C_{16}H_{10}O_5$, is prepared by heating cinnamic acid (10 parts), gallic acid (12 parts), and sulphuric acid (150 parts) at 45—55°, for two to three hours. The product is poured into water, filtered, and the precipitate washed with slightly acidified boiling water. It crystallises in bright-yellow, microscopic needles, which do not melt at 350°; it is very sparingly soluble, except in boiling alcohol, aniline, and glacial acetic acid, and sublimes when carefully heated in large, yellow, lustrous needles. Alkalis dissolve it with green colour, which changes to blue, and then red, when the solution is heated. The solution in sulphuric acid is yellowish-red. When oxidised with dilute nitric acid, it yields a large amount of phthalic acid. The *triacetyl-derivative*, $C_{22}H_{16}O_8$, crystallises in pale-yellow needles. With mordants, styrogallol yields shades similar to those obtained with nitroalizarin. N. H. M.

Paradiphenoldicarboxylic Acid. By R. SCHMITT and C. KRETZSCHMAR (*Ber.*, **20**, 2703—2704).—*Paradiphenoldicarboxylic acid*, $COOH{\cdot}C_6H_3(OH){\cdot}C_6H_3(OH){\cdot}COOH$, is obtained when sodium paradiphenol is heated in an autoclave with liquid carbonic anhydride at 200° for nine hours, and the resulting product is treated with an acid. It crystallises in small, microscopic needles, melts at 131° with the evolution of carbonic anhydride, is not volatile with steam, has a slightly bitter taste, and is readily soluble in ethyl and methyl alcohol and in ether, sparingly soluble in water (100 c.c. of water at 15° dissolving 0·0052 gram of the acid), and insoluble in benzene and chloroform. Suspended in water, it is coloured bluish-violet with ferric chloride, the colour changing to a dull brown on heating, whilst the sodium salt when similarly treated yields a deep blue solution, from which indigo-blue flocks separate. W. P. W.

Orthamidotriphenylmethane. By O. FISCHER and A. FRÄNKEL (*Annalen*, **241**, 362—368).—The preparation of diphenylquinolylmethane has been previously described by the authors (Abstr., 1886, 561). The sulphate and picrate are precipitated on the addition of sulphuric or picric acid to alcoholic solutions of the base. The nitro-derivative melts at 213° with decomposition, and the amido-compound on oxidation forms a violet-coloured solution.

Triphenylmethaneorthocarboxylic acid is prepared by slowly adding a solution of the hydrochloride of the diazo-compound of amidotriphenylmethane to a solution of potassium cyanide and copper sulphate at 90°. The crude product is saponified with alcoholic potash, and the acid precipitated from the aqueous solution of the potassium salt by hydrochloric acid. Alcohol, ether, acetic acid, and benzene dissolve the acid freely. It melts at 162° and volatilises without decomposition; it is identical with the acid Baeyer (Abstr., 1880, 650) obtained from phthalophenone.

Orthohydroxytriphenylmethane is formed by passing air through a solution of diazoamidotriphenylmethane sulphate, and boiling the product in a current of carbonic anhydride. It is soluble in alcohol and ether, and melts at 118°.

The acetic derivative of amidotriphenylmethane melts at 168—169°, and is freely soluble in alcohol, benzene, and acetic acid. The *thiocarbamide* melts at 123°, and dissolves readily in ether, carbon bisulphide, and hot alcohol. W. C. W.

Two Dihydroxynaphthalenes. By A. Emmert (*Annalen*, **241**, 368—373).—β-Naphthol yields two sulphonic acids on treatment with sulphuric acid, and each acid is converted into a dihydroxynaphthalene by fusion with potash.

β-β-Dihydroxynaphthalene melts at 215—216°, and dissolves freely in alcohol and ether. Ferric chloride produces a yellowish-white precipitate. At 120° alcoholic potash and ethyl iodide convert the dihydroxynaphthalene into an ethyl ether, $C_{10}H_6(OEt_2)$. It forms silky plates and melts at 162°. The *diacetate*, $C_{10}H_6(OAc)_2$, melts at 175°.

β-α-Dihydroxynaphthalene is soluble in alcohol, ether, benzene, and water. It melts at 178°, and gives a blue precipitate with ferric chloride. The diethyl ether crystallises in prisms, melting at 67°, and the diacetate forms rhombic plates and melts at 108°. W. C. W.

Derivatives of Di-β-naphthylamine. By C. Ris (*Ber.*, **20**, 2618—2628).—Crude di-β-naphthylamine is purified by distillation and crystallisation from benzene; it melts at about 471°.

Methyldi-β-naphthylamine, $NMe(C_{10}H_7)_2$, is prepared by heating dinaphthylamine and methyl iodide (equal molecular weights) for five hours at 150°, and crystallises from alcohol in nearly colourless needles melting at 139—140°. It dissolves rather readily in warm alcohol, glacial acetic acid, benzene, and ether, and is almost insoluble in light petroleum. The alcoholic solution shows a bluish-violet fluorescence. It is insoluble in dilute mineral acids; the *hydrochloride* forms slender, lustrous crystals, which decompose quickly in presence of water. The solution in strong sulphuric acid is yellow, and acquires an intense brown colour on addition of a trace of a nitrite or nitrate.

Ethyldi-β-naphthylamine, $NEt(C_{10}H_7)_2$, crystallises in almost colourless prisms melting at 231°; it resembles the methyl compound in solubility; the *hydrochloride* is a white, crystalline powder.

Methyl di-β-naphthylcarbamate, $N(C_{10}H_7)_2·COOMe$, is obtained by heating di-β-naphthylamine and methyl chloroformate (equal weights) at 150—160° for two and a half hours. It crystallises from alcohol in slender, white needles, melting at 113—114°, dissolves readily in alcohol, ether, and benzene. It crystallises from benzene with ½ mol. C_6H_6. It distils almost without decomposition.

Tetrabromodi-β-naphthylamine, $C_{20}H_{11}Br_4N$, is prepared by the action of bromine (4 mols.) on a well-cooled solution of di-β-naphthylamine in glacial acetic acid. It crystallises in long, white, matted needles, which melt at 245—246°. It dissolves rather readily in hot benzene and cumene, very sparingly in ether, light petroleum, and alcohol.

It is not attacked by boiling concentrated aqueous potash; bromine does not act on it.

Octobromodi-β-naphthylamine, $C_{20}H_7Br_8N$, is formed when β-dinaphthylamine, as dust, is added to an excess of bromine in presence of aluminium bromide. The product is stirred well, and the yellow precipitate, after being treated with alkali and with boiling hydrochloric acid to remove adhering bromine and aluminium, is crystallised from cumene. It forms slender, white needles, which melt at about 300°, and dissolve readily in boiling nitrobenzene, less in boiling cumene; in other solvents it is sparingly or not at all soluble.

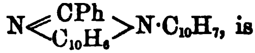
Nitrosodi-β-naphthylamine, $NO{\cdot}N(C_{10}H_7)_2$, is prepared by adding the calculated amount of sodium nitrite dissolved in a little water to a mixture of alcohol and sulphuric acid containing di-β-naphthylamine in the form of dust. It crystallises from benzene in groups of white needles, melting at 139—140°, sparingly soluble in alcohol, readily in benzene.

Dinitrodi-β-naphthylamine, $C_{20}H_{13}N(NO_2)_2$, is formed when strong nitric acid is slowly added to a cooled solution of the amine in glacial acetic acid; it separates after some time as a yellow powder. It crystallises in yellowish-red needles, melting at 224—225°, readily soluble in boiling cumene, less soluble in benzene, and almost insoluble in alcohol and ether.

Tetranitrodi-β-naphthylamine, $C_{20}H_{11}N(NO_2)_4$, is obtained by gradually adding nitric acid (3 parts) mixed with glacial acetic acid to a solution of dinaphthylamine (1 part), in glacial acetic acid. It crystallises from nitrobenzene in grains, which melt at 285—286°, and detonate when more strongly heated. It is sparingly or not at all soluble in the ordinary solvents, readily soluble in boiling nitrobenzene.

Hexanitrodi-β-naphthylamine, $C_{20}H_9N(NO_2)_6$, prepared by heating the finely-powdered amine with fuming nitric acid, could not be obtained in crystals. It dissolves readily in alcohol, less in glacial acetic acid, and is almost insoluble in ether, benzene, cumene, and nitrobenzene. Alkaline carbonates dissolve it readily. When mixed with excess of copper oxide, it decomposes with explosive violence, and was therefore not analysed. The *potassium* and *barium salts* were analysed; they are both amorphous.

Benzoylorthonitrodi-β-naphthylamine, $C_{27}H_{18}NO{\cdot}NO_2$, is prepared by adding a mixture of fuming nitric and sulphuric acids to a solution of benzoyldi-β-naphthylamine in cold glacial acetic acid, and subsequently heating the whole at 50—60°. It crystallises from benzene in well-formed, yellow, transparent crystals (with 1 mol. C_6H_6), melting at 95°. Crystallised from alcohol it melts at 168°. It dissolves readily in warm benzene, less in alcohol.

Benzenylnaphthyleneamidine,  $N{<}{\genfrac{}{}{0pt}{}{CPh}{C_{10}H_6}}{>}N{\cdot}C_{10}H_7$, is obtained by reducing benzoylnitrodinaphthylamine dissolved in glacial acetic acid with excess of tin and hydrochloric acid. It crystallises from benzene in transparent, slender needles (with 1 mol. C_6H_6) melting at 113—114°; when crystallised from other solvents it melts at 163°. It sublimes when carefully heated in small, colourless plates, and distils with slight decomposition. It is readily soluble. The *hydrochloride* forms slender, matted needles which decompose in contact with water.

N. H. M.

Naphthaphenazine. By P. BRUNNER and O. N. WITT (*Ber.*, **20**, 2660—2663). — *Naphthaphenazinesulphonic acid* is obtained when naphthaphenazine is heated with 10 times its weight of 35 per cent. fuming sulphuric acid at 100° for 12 hours. It crystallises in orange-red needles, melts above 290°, and is soluble in water and alcohol. In concentrated sulphuric acid it dissolves with a deep orange-brown colour, which becomes orange-yellow on dilution. The *sodium* salt, $C_{16}H_9N_2\cdot SO_3Na + 2H_2O$, was prepared. On fusion with potassium hydroxide, a *eurhodol* is obtained which differs from that previously described (Abstr., 1887, 153), since it dissolves in hydrochloric acid with a red colour, and in concentrated sulphuric acid with a dark-green colour changing to red on dilution. A similar compound has been prepared by diazotising the eurhodine formed by the reduction of nitronaphthaphenazine.

Cyanonaphthaphenazine, $C_{16}H_9N_2\cdot CN$, is obtained when sodium naphthaphenazinesulphonate is distilled with potassium cyanide or dry potassium ferricyanide. Crystallised from cumene, it melts at 236—237°, and dissolves in concentrated sulphuric acid with a cherry-red colour, which changes through orange to yellow on dilution. If heated with hydrochloric acid under pressure, it is decomposed into naphthaphenazine and formic acid, but when heated with alcoholic potash at 220—230° it is partially converted into *naphthaphenazinecarboxylic acid*. This is sparingly soluble in the ordinary solvents, melts above 360°, and dissolves in concentrated sulphuric acid with a deep-red colour, changing to yellow on dilution. The *potassium* salt crystallises in white needles and is sparingly soluble in water.

W. P. W.

Naphtholcarboxylic Acids. By R. SCHMITT and E. BURKARD (*Ber.*, **20**, 2699—2704).—*α-Naphtholcarboxylic acid* (m. p. 187°) can be prepared by heating sodium α-naphthol with liquid carbonic anhydride in an autoclave at 130°, and is a comparatively stable compound (compare Abstr., 1887, 732), since it is only partially decomposed by prolonged boiling with water, in which it is very sparingly soluble. The aqueous solution is coloured greenish-blue by ferric chloride. The *sodium* salt, with 3 mols. H_2O, crystallises in large, thin, nacreous scales; the *ammonium* salt forms long needles; the *calcium* and *barium* salts crystallise in long needles. The *methyl* salt, $OH\cdot C_{10}H_6\cdot COOMe$, melts at 78°, the *ethyl* salt at 49°, and the *phenyl* salt at 96°. The *acetyl*-derivative, $OAc\cdot C_{10}H_6\cdot COOH$, melts at 158°; the *bromo*-derivative, $OH\cdot C_{10}H_5Br\cdot COOH$, melts at 238°; the *nitro*-derivative,

$$OH\cdot C_{10}H_5(NO_2)\cdot COOH,$$

melts at 202°, and yields β-nitro-α-naphthol when heated with lime; the *amido*-derivative melts above 200°, and its *acetyl*-compound at 185°. Metadiazonaphtholcarboxylic acid, $OH\cdot C_{10}H_5\Big<\genfrac{}{}{0pt}{}{COO}{N:N}\Big>$, and parazobenzenesulphonic acid-α-naphtholcarboxylic acid,

$$SO_3H\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(OH)\cdot COOH,$$

were also obtained, and the latter on reduction with zinc and hydrochloric acid yields an amido-α-naphtholcarboxylic acid which crystallises in colourless, prismatic needles, is very sparingly soluble in water, and melts above 200°, but differs from the amido-derivative just described since its *acetyl*-compound melts at 195°.

When sodium β-naphthol is similarly heated with liquid carbonic anhydride in an autoclave at 130°, *β-naphtholcarboxylic acid* is obtained, and is separated by treating the product with ammonium carbonate and precipitating with hydrochloric acid. This acid readily decomposes on heating, and shows all the properties of Kauffmann's acid (Abstr., 1882, 1068). Ferric chloride colours its aqueous solution a pure blue. The *ammonium* salt crystallises in yellow needles, whilst the *barium*, *calcium*, and *silver* salts resemble the corresponding salts of the α-acid. The *methyl* salt melts at 76°, and the *ethyl* salt at 55°.

When sodium β-naphthol is heated at 280—290° in a current of carbonic anhydride, absorption of the gas rapidly takes place, and a product is obtained consisting of β-naphthol, undecomposed sodium β-naphthol, and *β-naphtholcarboxylic acid.* This acid is extremely stable, and crystallises from water in lustrous, rhombic, yellow scales, which melt at 216° without decomposition, and are readily soluble in alcohol and ether, soluble in toluene, benzene, and chloroform, and sparingly soluble in hot water. Ferric chloride colours the aqueous solution blue. W. P. W.

Terpenes. Part VI. By O. WALLACH (*Annalen*, **241**, 315—328). —The compound which the author (Abstr., 1887, 967) recently described as terpene nitrite is *terpinene nitrosite.* It forms monoclinic crystals; $a : b : c = 1{\cdot}0103 : 1 : 0{\cdot}66978$; $\beta = 80° 31'$.

Terpinene nitrolethylamine, $NHEt{\cdot}C_{10}H_{15}\colon NOH$, is obtained by boiling for a short time an alcoholic solution of the nitrosite with a strong aqueous solution of ethylamine. The crude product is poured into water, the precipitate dissolved in hydrochloric acid, and the base reprecipitated by ammonia. The base melts at 130—131°, and dissolves in boiling alcohol, ether, chloroform, and in warm dilute solutions of alkalis. The *hydrochloride*, $C_{12}H_{22}N_2O,HCl$, is crystalline, and dissolves freely in water and alcohol. The nitroso-compound melts at 132—133°. It is decomposed by boiling with an excess of hydrochloric acid, yielding hydroxylamine.

Terpinene nitroldiethylamine, $NEt_2{\cdot}C_{10}H_{15}\colon NOH$, melts at 117—118°.

Terpinene nitrolmethylamine, $NHMe{\cdot}C_{10}H_{15}\colon NOH$, crystallises in prisms and melts at 141°. The *dimethylamine*, $NMe_2{\cdot}C_{10}H_{15}\colon NOH$, melts at 160—161°. It dissolves in chloroform.

The *amylamine*-compound is less soluble in alcohol and ether than the preceding substances. It melts at 118—119°. The *piperidine*, $C_{10}H_{16}NO,NC_5H_{10}$, melts at 153—154°. It is insoluble in alkalis, but its salts are freely soluble in water. The hydrochloride is obtained as an oil on passing dry hydrogen chloride into an ethereal solution of the base.

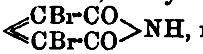
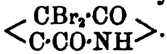
Terpinene nitrolamine is formed by adding ammonia to a hot alcoholic solution of terpinene nitrosite. After recrystallisation from hot water it melts at 116—118°.

By adding a mixture of nitric acid and amyl nitrite to carvene or citronene saturated with dry hydrogen chloride, Maissen (*Gazzetta*, **13**, 99) obtained a crystalline compound melting with decomposition at 114—115°. The author has obtained the same or similar derivatives from cinnamene and dipentene. They melt at 109° and 110—111° respectively, and act on organic amines, yielding crystalline bases. W. C. W.

Constitution of some Pyrroline-derivatives. By G. Ciamician and P. Silber (*Ber.*, **20**, 2594—2607; compare Abstr., 1887, 597). —*Dibromodiacetylpyrroline*, $C_4NHAc_2Pr_2$, is prepared by the action of bromine vapour on a warm solution of 2 grams of pyrrylenedimethyldiketone in 700 c.c. of water. It crystallises from alcohol in white needles melting at 171—172°, insoluble in water, soluble in alcohol, ether, and in alkaline carbonates. Nitric acid oxidises it readily at the ordinary temperature to dibromomaleïmide; the constitution of the base is therefore $[Br_2 : Ac_2 = 3 : 4 : 2 : 5]$.

Nitrodibromacetylpyrroline, $C_4NHBr_2Ac{\cdot}NO_2$ $[Br_2 : Ac : NO_2 = 3 : 4 : 2 : 5]$, is formed when dibromodiacetylpyrroline (8 grams) is dissolved in fuming nitric acid (80 grams), and crystallises from alcohol in long, white needles melting at 206°. It is soluble in alcohol, ether, ethyl acetate, hot glacial acetic acid, and benzene, very sparingly soluble in water, insoluble in light petroleum. Alkaline carbonates dissolve it readily with intense yellow colour.

Dinitrodibromopyrroline, $C_4NHBr_2(NO_2)_2$ $[= 3 : 4 : 2 : 5]$, is obtained by the action of a well-cooled mixture of sulphuric and fuming nitric acids on the mononitro-compound. It crystallises from water in large, yellow plates (with 1 mol. H_2O), which melt at about 169° with decomposition; it is readily soluble in ether, alcohol, hot water, and hot benzene, and dissolves in alkaline carbonates with evolution of carbonic anhydride. If the mixed acids are allowed to act on the mononitro-compound at the ordinary temperature, dibromomaleamide, melting at 227°, is formed. The latter is also formed when dinitrodibromopyrroline is heated at 165°; nitric oxide is evolved.

When dinitrodibromopyrroline is heated with sulphuric acid (20 parts) it is converted quantitatively into dibromomaleïc acid. It is probable that the imide of dibromomaleïc acid, and, therefore, maleïc acid also, are symmetrically rather than unsymmetrically constituted:  $<\begin{matrix}\mathrm{CBr{\cdot}CO}\\ \mathrm{CBr{\cdot}CO}\end{matrix}>\mathrm{NH}$, rather than  $<\begin{matrix}\mathrm{CBr_2{\cdot}CO}\\ \mathrm{C{\cdot}CO{\cdot}NH}\end{matrix}>$. (Compare Anschütz, Abstr., 1887, 916).

Dibromopyrrolinedicarboxylic acid behaves towards fuming nitric acid in a manner similar to dibromodiacetylpyrroline; dinitrodibromopyrroline $[NO_2 : NO_2 : Br : Br = 2 : 5 : 3 : 4]$ is formed identical with that obtained from dibromodiacetylpyrroline. The reaction shows that the two carboxyl-groups in pyrrolinedicarboxylic acid have the positions 2 : 5.

Methyl dibromopyrrolinedicarboxylate, $C_4NHBr_2(COOMe)_2$, is obtained by dissolving methyl pyrrolinedicarboxylate (3 grams) in water (1 litre), and saturating the lukewarm solution with bromine vapour. The yield is 4·5 grams of pure product. It crystallises from alcohol in long, white needles, melting at 222°, soluble in ether, almost insoluble in water. When 2 grams of the salt is added to 40 grams of fuming nitric acid at −18°, and the whole poured into 400 c.c. of ice-water, and treated with potash (30 grams), the *compound* $C_4H_4BrNO_4$ is obtained. It is a crystalline compound, melting at 168—171° with decomposition, soluble in ether, alcohol, and hot benzene, rather sparingly soluble in water, and insoluble in light petroleum. It dissolves in alkaline carbonates with evolution of carbonic anhydride. The constitutional formula $CBrO{\cdot}C(NOH){\cdot}COOMe$ is suggested for it.

Methyl dibromacetylcarbopyrrolate, $C_4NHBr_2Ac{\cdot}COOMe$, is prepared in a manner similar to the methyl salt of the bromodicarboxylic acid, which it completely resembles in its behaviour towards fuming nitric acid.

Dibromacetylmethylpyrroline, $C_7H_7Br_2NO$, is prepared by treating a solution of 2 grams of acetylmethylpyrroline, melting at 85—86° (Abstr., 1886, 719), with an excess of bromine. It crystallises from dilute alcohol in long, white needles, of a silky lustre, melts at 161—162°, dissolves in ether, carbon bisulphide, and chloroform, and is sparingly soluble in boiling water. When the finely-powdered compound is warmed with fuming nitric acid, dibromomaleïmide (m. p. 227°) is formed. The constitution of acetylmethylpyrroline is therefore [Ac : Me = 2 : 5].

In order to obtain further evidence as to the constitution of pyrvyl methyl ketone and Schwanert's carbopyrrolic acid, tribromacetylpyrroline and methyl tribromocarbopyrrolate were converted into dibromomaleïmide by the action of nitric acid.

Dibromonitracetylpyrroline, $C_4NHBr_2Ac{\cdot}NO_2$ [Br : Br : Ac : NO_2 = 2 : 3 : 5 : 4], is prepared by the action of bromine on nitracetylpyrroline, melting at 197° (Abstr., 1885, 810 and 992). It crystallises from alcohol in needles melting at 175°, soluble in ether, warm alcohol, and glacial acetic acid, sparingly soluble in warm water, insoluble in light petroleum. The non-identity of this compound with the dibromo-derivative described above, and the probability that in the nitracetyl-compound (m. p. 197°) the acetyl-group has the α-position, make it probable that the nitracetyl-compound has the constitution [NO_2 : Ac = 3 or 4 : 2 or 5].

A table of all pyrroline-derivatives (halogen-derivatives and ethers excepted) of known constitution is given. N. H. M.

Synthesis of Pyridine and Piperidine-derivatives. By C. PAAL and C. STRASSER (*Ber.*, **20**, 2756—2766).—Diphenacylacetic acid (Abstr., 1887, 261) when treated with alcoholic ammonia yields the ammonium salt of *αα'-diphenyldihydropyridine-γ-carboxylic acid*, $C_5NH_4Ph_2{\cdot}COONH_4$. This salt is soluble in water and concentrated hydrochloric acid; on acidification with sulphuric acid, the corresponding acid separates, but is quickly decomposed. On dry distillation, ammonia is given off, and *αα'-diphenylpyridinecarboxylic acid*,

$\cdot C_5NH_2Ph_2\cdot COOH$, is produced, which after purification crystallises in delicate, white needles or prisms, melting at 275°, soluble in alcohol, sparingly soluble in chloroform. The acid is not altered by nitrous acid, acetic chloride, or oxidising agents. Its ammonium salt does not exist in the free state; the *silver* salt is a heavy, white precipitate; the *chromate* a dark-red, amorphous precipitate; the *aurochloride* is crystalline.

αα-Diphenylpiperidine-γ-carboxylic acid, $C_5NH_8Ph_2\cdot COOH$, obtained together with the above acid, and separated from it by its greater solubility, forms crystalline crusts; it melts at 339°, and sublimes without decomposition, its alkaline salts are very soluble, the *barium* and *silver* salts are white precipitates. Its *nitroso-derivative* crystallises in pale-yellow, glistening needles melting at 159°, and is soluble in ether and alcohol.

αα-Diphenylpyridine, C_5NH_3Ph, obtained by the distillation of the calcium salt of the carboxylic acid with lime, crystallises in long, glistening needles melting at 81—82°; its *platinochloride* forms yellow needles, and the *aurochloride* a crystalline precipitate; the *methiodide* crystallises in needles melting at 203°.

αα-Diphenylpiperidine, $C_5NH_9Ph_2$, obtained by the hydrogenation of the above base, is a thick, pale-yellow oil; its *hydrochloride* crystallises in white needles; the *platinochloride* and the *aurochloride* and the *nitroso-derivative* crystallise with difficulty. V. H. V.

3-Methylpyridine and 3-Methylpiperidine. By C. STOEHR (*Ber.*, **20**, 2727—2733).—The picoline obtained by distilling strychnine with lime (Abstr., 1887, 604) proves on further examination to be β-picoline, since nicotinic acid is found to be the sole product on oxidation with 2 per cent. permanganate solution. Some quantity of the base was prepared to enable an examination of its properties to be made, and the results are compared with those of previous observers. β-Picoline thus obtained boils at 145—150° after two fractionations; by conversion of this product into the mercurochloride and regeneration of the base, it gives a product which mostly passes over between 148° and 149° (compare Hesekiel, Abstr., 1885, 812). The platinochloride, $(C_6H_7N)_2,H_2PtCl_6 + H_2O$, has the properties of the salt described by Baeyer (*Annalen*, **155**, 285), melts when dry at 195°, loses 1 mol. H_2O when allowed to remain in a desiccator, and when heated at 120° loses in addition 1 mol. HCl, the compound thus obtained, $(C_6H_7N)_2,HCl,PtCl_4$, melting at 211—212°. The aurochloride melts at 182—183°. The mercurochloride, $C_6H_7N,HCl,2HgCl_2$ (compare Hesekiel, Abstr., 1886, 256), crystallises from hot water in slender, ramifying needles, from dilute hydrochloric acid in indented scales, or long, compact needles, and from concentrated hydrochloric acid, in which it is very soluble, in small, well-formed prismatic crystals melting at 139—140°. The picrate crystallises in six-sided scales melting at 142—143°.

3-Methylpiperidine, obtained by reduction of the β-picoline in alcoholic solution with sodium, is readily soluble in water, and yields a hydrochloride, crystallising in dazzling, white needles.

W. P. W.

2 : 6 Methylethylpyridine and 2 : 4 Methylethylpyridine. By M. SCHULTZ (*Ber.*, **20**, 2720—2727).—Picoline ethiodide, when heated at 280—300° for 1 to 1½ hours, yields a mixture of bases. To separate these, the product is treated with water, acidified, distilled to remove a small quantity of an aromatic oil, then rendered alkaline and again distilled. The mixture of bases so obtained, which boils between 100° and 200°, is fractionated, and the fractions boiling at 156—166°, 166—172°, and 172—182° repeatedly refractionated; in this way fractions boiling at 158—163° and 169—174° are obtained, and these consist chiefly of 2 : 6 methylethylpyridine and 2 : 4 methylethylpyridine respectively.

2 : 6 *Methylethylpyridine*, $C_8H_{11}N$, is a colourless, hygroscopic, oily liquid, having a sweet, aromatic odour recalling that of picoline, and when moist, an alkaline reaction. It is sparingly soluble in water, readily volatile with steam, and yields salts which readily deliquesce in air. The *platinochloride*, $(C_8H_{11}N)_2,H_2PtCl_6$, crystallises in tabular, triclinic crystals, melts at 173—174° (after drying at 110°), and is readily soluble in hot water, insoluble in alcohol and ether; the *aurochloride*, $C_8H_{11}N,HAuCl_4$, crystallises in yellow needles, melts at 110°, and is sparingly soluble in water, readily soluble in ether alcohol. On reduction with sodium in hot alcoholic solution, *copellidine*, $C_8H_{17}N$ [Me : Et = 2 : 6], is obtained; this is a colourless, oily liquid, which boils at 147—151°, fumes slightly in the air, has the characteristic odour of piperidine bases, and a strongly alkaline reaction. The *nitroso*-derivative is a brown oil; the *hydrochloride*, $C_8H_{17}N,HCl$, crystallises in white needles, and though readily soluble in water and alcohol is only slightly hygroscopic. When oxidised with 2 per cent. permanganate solution, 2 : 6 methylethylpyridine is converted into a dicarboxylic acid melting at 226°, and identical with Ladenburg and Roth's dipicolinic acid (Abstr., 1885, 557).

2 : 4 *Methylethylpyridine*, [Me : Et = 2 : 4], is a hygroscopic, colourless, oily liquid, which in its properties closely resembles the 2 : 6-derivative. The *platinochloride*, $(C_8H_{11}N)_2,H_2PtCl_6$, forms reddish-yellow, tabular crystals, which after drying at 110° melt at 190°; the *aurochloride*, $C_8H_{11}N,HAuCl_4$, crystallises in yellow needles, begins to fuse at 83°, melts at 90°, and is soluble in hot water, readily soluble in alcohol and ether. When the base is reduced with sodium in hot alcoholic solution, it is converted into *copellidine*, [Me : Et = 2 : 4] $C_8H_{17}N$; this is a colourless, oily liquid, which boils at 155—160°, has a strongly alkaline reaction, and an odour similar to that of the 2 : 6 base. The *hydrochloride*, $C_8H_{17}N,HCl$, crystallises in white needles, is readily soluble in water and alcohol, and is slightly hygroscopic. On oxidation with 2 per cent. permanganate solution in the cold or on heating, 2 : 4 methylethylpyridine yields a dicarboxylic acid whose melting point rose from 204° to 211° after three crystallisations. This author regards this acid as being identical with Ladenburg and Roth's lutidinic acid (Abstr., 1885, 815), and ascribes its lower melting point to the presence of a small quantity of picolinic acid. W. P. W.

Phenylated Piperidine and Pyridine Bases. By O. BALLY (*Ber.*, **20**, 2590—2594).—*γ-Phenylpiperidine*, $C_5NH_{10}Ph$, is prepared from γ-phenylpyridine and purified by distillation. It melts at 57·5—58°, and boils at 255—257° under 727 mm. pressure; it is a strong base, almost insoluble in water. The salts are readily soluble. The *hydrochloride* crystallises in needles; the *platinochloride* forms orange-coloured plates, melting at 204—207°. It gives no precipitate with picric acid; the original base gives a precipitate even in very dilute solution.

Phenyllutidine, $C_5NH_2Me_2Ph$ [Me : Ph : Me = 2 : 4 : 6], is obtained by distilling potassium phenyllutidinecarboxylate (prepared from benzaldehyde, ethyl acetoacetate, and ammonia) with lime, at the lowest possible temperature. It is purified by means of the hydrochloride, and crystallises from ether in prisms melting at 54·5—55°. It boils at 287° under 731 mm. pressure. The salts are generally sparingly soluble; the *hydrochloride* (with 3 mols. H_2O) crystallises in slender, matted needles which do not melt at 300°; the *platinochloride*, $(C_{13}H_{13}N)_2,H_2PtCl_6 + 4H_2O$, forms orange-coloured needles; the *nitrate* and *chromate* melt at 177° and 222° respectively, both crystallise in needles.

γ-Phenyllupetidine, $C_5NH_8PhMe_2$, is prepared by the action of sodium (2·5 parts) on phenyllutidine (1 part) dissolved in absolute alcohol; it is separated from unchanged phenyllutidine by distillation. It is a colourless oil of a peculiar odour, boiling at 274° under 731 mm. pressure. The *hydrochloride* and *nitrate* crystallise in prisms; the *dinitrate* melts at 210°; the *platinochloride* crystallises in gold-coloured plates melting at 237°. Besides phenyllupetidine, a compound, probably *heptylbenzene*, $CHPh(CH_2{\cdot}CH_2Me)_2$, is produced in the reduction of phenyllutidine.

When *γ-phenyllutidylium methiodide* (prepared by digesting the base with methyl iodide in a reflux apparatus) is treated with strong aqueous potash, a base is obtained which yields a hydrochloride identical with that formed by the action of silver chloride on methylphenyllutidylium iodide.

Methyl-γ-phenyllutidylium iodide is a crystalline substance sparingly soluble in hot water. N. H. M.

α-Cinnamylpyridine. By H. BAURATH (*Ber.*, **20**, 2719—2720).—When α-picoline and benzaldehyde in equimolecular proportions are heated with zinc chloride at 220—225° for six hours, *α-cinnamylpyridine*, $C_5NH_4{\cdot}CH:CHPh$, is obtained, and after removal of unaltered benzaldehyde by steam distillation can be separated by rendering the product alkaline and distilling with superheated steam. The base, already prepared but not described by Jacobsen and Reimer (Abstr., 1884, 335), is crystalline, melts at 90·5—91°, boils at 313—314° (uncorr., under 753 mm. pressure), and is readily soluble in carbon bisulphide and ether, soluble in alcohol, benzene, and light petroleum, and practically insoluble in water. The salts generally crystallise in needles: the *platinochloride*, $(C_{13}H_{11}N)_2,H_2PtCl_6 + 2H_2O$, decomposes when heated to expel the water of crystallisation. On treatment with bromine in carbon bisulphide solution, the base yields an additive compound, $C_{13}H_{11}NBr_2$, which crystallises from alcohol in compact needles melting at 166—167°; this derivative yields a new base when heated with alcoholic potash. Derivatives of α-cinnamylpyridine have also been obtained by the action of hydriodic acid and by reduction of sodium and alcohol, and will be described in a later communication. W. P. W.

Ethylquinoline. By L. Reher (*Ber.*, **20**, 2734—2735).—Doebner having found the boiling point of α-ethylquinoline to be 245—246° (Abstr., 1887, 504), the author has redetermined the boiling points of α- and γ-ethylquinoline (*ibid.*, 279) by converting the bases into the platinochlorides, recrystallising these repeatedly from concentrated hydrochloric acid, and regenerating the bases from the pure salts by means of hydrogen sulphide. α-Ethylquinoline boils at 256·6—258·6° (corr.) and γ-ethylquinoline boils at 271—274° (corr.), and the pure platinochlorides melt at 189° and 203° respectively. From the pure bases, *chromates* were prepared crystallising in red needles, and crystalline *zincochlorides* were also obtained, that of the γ-base forming white, concentrically-grouped needles melting at 195°.

Diethylquinoline, obtained by the decomposition of the mercurochloride (*loc. cit.*), is a colourless liquid having a quinoline-like odour, and boiling at 282·8—284·8° (corr.). The *platinochloride*, $(C_9H_5NEt_2)_2,H_2PtCl_6$, crystallises in orange-red needles, and melts at 217° after previous blackening. On oxidation with chromic acid, the base yields a small quantity of an acid which crystallises in asbestos-coloured needles melting at 190°. W. P. W.

Orthohydroxyquinolinecarboxylic Acid. By R. Schmitt and F. Engelmann (*Ber.*, **20**, 2690—2695).—Further examination of orthohydroxyquinolinecarboxylic acid (Abstr., 1887, 738) shows that it begins to fuse at 137°, that carbonic anhydride and orthohydroxyquinoline are formed at 144—145°, and that the decomposition is complete at 150°. The *ammonium* salt, $OH{\cdot}C_9NH_5{\cdot}COONH_4 + H_2O$, crystallises in glistening, pale-yellow needles, and is soluble in water; the *barium* salt, $(OH{\cdot}C_9NH_5{\cdot}COO)_2Ba + 2H_2O$, crystallises in long, silky needles, and is sparingly soluble in water; the *calcium* salt crystallises in stellate groups of prisms; a basic barium salt, $C_{10}NH_5O_3Ba$, and a basic calcium salt were also prepared; the former is very sparingly soluble in water. The *phenyl* salt, $OH{\cdot}C_9NH_5{\cdot}COOPh$, obtained by heating equimolecular proportions of the acid and phenol at 170°, forms colourless, short prisms and melts at 225—226°. The *hydrochloride* of the acid, $OH{\cdot}C_9NH_5{\cdot}COOH,HCl$, crystallises in large prisms, and the *nitrate* in yellow needles; both salts are decomposed by water. On treatment with strong nitric acid, a dinitrohydroxyquinoline is obtained which is probably identical with that described by Bedall and Fischer (Abstr., 1881, 613; *Ber.*, **14**, 1368); it crystallises in golden-yellow scales, melts at 276° with blackening and the evolution of gas, is sparingly soluble in most solvents, and readily decomposes alkaline carbonates, forming the corresponding salts.

Nitrohydroxyquinolinecarboxylic acid, $NO_2{\cdot}C_9NH_4(OH){\cdot}COOH$, is prepared by heating the nitrate of orthohydroxyquinolinecarboxylic acid with acetic acid at 100°; the resulting brown mass is extracted with acetic acid until it becomes yellow, and is then purified by solution in hydrochloric acid and subsequent precipitation with water. It crystallises from water in yellow needles showing a vitreous lustre, decomposes at 200° with the evolution of carbonic anhydride, and dissolves readily in concentrated hydrochloric acid, in alkalis and in alkaline carbonates, but is sparingly soluble in acetic acid. When heated above 200°, *nitrohydroxyquinoline*, $NO_2\cdot C_9NH_5\cdot OH$, is formed; this crystallises in yellow needles, melts at 173°, is readily soluble in acetic acid and hot hydrochloric acid, less so in alcohol and ether. On treatment with bromine (2 mols.) at 100°, a dibromohydroxyquinoline identical with that prepared by Bedall and Fischer (*loc. cit.*) is obtained together with *bromohydroxyquinolinecarboxylic acid*, $OH\cdot C_9NH_4Br\cdot COOH$; this crystallises in matted, citron-yellow needles, melts at 233—235° with the evolution of carbonic anhydride, and yields a hydrochloride which crystallises in well-formed tables, and decomposes when boiled with water. *Bromohydroxyquinoline*, $C_9NH_5Br\cdot OH$, formed quantitatively when the bromo-acid is heated at 200°, crystallises in white needles, melts at 119—120°, and is readily soluble in the ordinary solvents except water.

W. P. W.

Parahydroxyquinolinecarboxylic Acid. By R. SCHMITT and J. ALTSCHUL (*Ber.*, 20, 2695—2698).—When potassium parahydroxyquinoline is heated with liquid carbonic anhydride in an autoclave at 170° for six to seven hours, a quantitative yield of potassium parahydroxyquinolinecarboxylate is obtained; the sodium-compound cannot be substituted for the potassium-derivative in this reaction. *Parahydroxyquinolinecarboxylic acid*, $OH\cdot C_9NH_5\cdot COOH$, crystallises from water in yellowish-white flocks consisting of microscopic prisms, melts at 203—204° with the evolution of carbonic anhydride and formation of parahydroxyquinoline, and is sparingly soluble in alcohol, ether, benzene, and hot water. Ferric chloride colours the aqueous solution red. The *hydrochloride*, $OH\cdot C_9NH_5\cdot COOH,HCl$, crystallises in long, colourless needles, or from concentrated hydrochloric acid in short, thick prisms, is decomposed by water, and yields a well-crystallised platinochloride; the *nitrate*, formed by digesting the acid with nitric acid (sp. gr. = 1·35), crystallises in large, white needles, and is decomposed by water. The *ammonium* salt, with ½ mol. H_2O, crystallises in long, colourless needles, and is soluble in water, the solution evolving ammonia when boiled; the *barium* salt, with 2 mols. H_2O, crystallises in colourless tufts of needles, and does not form a basic salt when treated with barium hydroxide.

If the nitrate of parahydroxyquinolinecarboxylic acid is heated with nitric acid, yellowish-red prisms separate on cooling, which when treated with water decompose into nitric acid and nitrohydroxyquinoline; this crystallises in yellow needles, melts at 136°, and is probably identical with Skraup's nitrohydroxyquinoline (Abstr., 1882, 92).

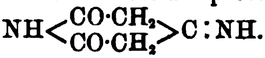
W. P. W.

Constitution of Glutazine. By H. v. PECHMANN (*Ber.*, 20, 2655—2658; compare Abstr., 1887, 155).—*Nitroglutazine*, $C_5H_5N_2O_2\cdot NO_2$, is obtained together with dinitroglutazine when nitrous oxide is passed into a cold aqueous solution of glutazine. It crystallises from water in orange-yellow plates which decompose at 170—180° without melting. *Dinitroglutazine*, $C_5H_4N_2O_2(NO_2)_2$, crystallises from water in yellow plates. Both compounds give colourless solutions with acetic acid and zinc-dust which become red when exposed to air. When heated with alkali, they are converted, with evolution of ammonia, into sparingly soluble salts which crystallise in sulphur-coloured, matted needles and explode when heated. These results make it improbable that glutazine contains an amido-group.

The *nitronitrosamine*, $NO_2{\cdot}C_5H_4N_2O_2{\cdot}NO$, is obtained when glutazine (1 part) dissolved in the smallest amount of dilute aqueous soda is treated with sodium nitrite (1 part); water is added (so that the whole amounts to 30 parts), and the whole is poured into a mixture of glacial acetic acid (5 parts) and water (30 parts). In a short time it solidifies to an orange-coloured magma. The *sodium salt*, $C_5H_3NaN_4O_5$, so obtained crystallises in yellow needles with water of crystallisation. Acids precipitate greenish-yellow needles from the solution. When the sodium salt dissolved in glacial acetic acid is warmed with excess of sodium nitrite, the *sodium salt* of the *dinitronitrosamine*, $C_5H_2NaN_5O_7$, separates as a cinnabar-coloured, crystalline powder. This dissolves sparingly in water, readily in alkalis. When warmed with dilute acids nitrous acid is given off.

Dibenzoylglutazine, $C_5H_4N_2O_2Bz_2$, is obtained by heating glutazine with benzoic chloride on a water-bath for two to three hours, and crystallises from glacial acetic acid in lustrous, brownish plates melting at 215—216°. It is insoluble in water and in alkalis, sparingly soluble in alcohol.

The above results show that there are only two hydrogen-atoms in glutazine displaceable by acid radicles, and that these are present as imidohydrogen as shown by the formula



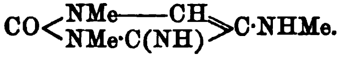
$$NH\lessdot\begin{matrix}CO{\cdot}CH_2\\CO{\cdot}CH_2\end{matrix}\gtrdot C\colon NH.$$

N. H. M.

Reactions of Caffeïne and Caffeïdine. By M. WERNECKE (*Chem. Centr.*, 1887, 1082—1084).—Hydriodic acid, like hydrochloric acid, decomposes caffeïne into carbonic oxide and anhydride, formic acid, sarcosine, ammonia, and methylamine; if phosphorus is added, glycocine is formed instead of sarcosine, whilst hydrogen phosphide and phosphonium iodide are evolved. Although methyl iodide readily combines with caffeïne to form the methiodide, the formation of the corresponding ethyl-compound presents considerable difficulty. Phenylhydrazine will not combine with caffeïne; from this it would seem that in this case, as an analogue of carbamide, the carbonyl-group is directly combined with the nitrogen-atom.

Caffeïne chloriodide, $C_8H_{10}N_4O_2,ClI$, is produced when sodium nitrite and potassium iodide are added to a hydrochloric acid solution of this base; it forms golden needles melting at 182—183°, and is decomposed into its constituents by ammonia or by boiling with water. The method proposed by Maly and Andreasch for the preparation of caffeïdine presents no advantage over that of Strecker. Caffeïne sulphate differs from the hydroiodide in that the former, when heated, turns purple-red, whilst the latter yields a green mass; the aurochloride of caffeïne cannot be isolated. The base is best separated from the sulphate by means of basic lead carbonate. *Methylcaffeïdine hydriodide* is not a well-defined substance, but the free base is crystalline and melts at 86—88°; *dimethylcaffeïdine* forms leaflets melting at 123°.

The author ascribes the following constitution to caffeïdine,



$$CO\left\langle\begin{matrix}NMe\text{———}CH\\NMe\cdot C(NH)\end{matrix}\right\rangle C\cdot NHMe.$$

V. H. V.

Hydroquinine. By O. Hesse (*Annalen*, **241**, 255—287).—*Hydroquinine*, $C_{20}H_{26}N_2O_2$, exists ready formed in cinchona bark, and is present in varying quantities in commercial quinine. It is conveniently prepared from the mother-liquor obtained in the manufacture of the acid sulphate of quinine. The mother-liquor is neutralised and the neutral salt dissolved in sulphuric acid, quinine monosulphate crystallises, and the mother-liquor containing the hydroquinine is again neutralised. By repeating these operations a salt is obtained containing 30 per cent. of hydroquinine sulphate. The quinine is removed by oxidising the solution in sulphuric acid with potassium permanganate, the mixture is filtered and the hydroquinine liberated by the addition of an alkali and extracted with ether. The base is deposited from its solution in chloroform in needles and from hot acetone in long plates. Many of the properties of the compound have been previously described by the author (Abstr., 1882, 1113). It is lævogyrate $[\alpha]_D = -142{\cdot}2°$ for a 2·4 per cent. solution in 95 per per cent. alcohol at 20°, and $[\alpha]_D = -227{\cdot}1°$ for an aqueous solution of the same strength under similar conditions. (40 c.c. normal hydrochloric acid were contained in each 100 c.c. of water used for the solution.) When ammonia is added to a solution of equal molecular proportions of cupreïne and hydroquinine in water containing sulphuric acid, and the acid mixture extracted with ether, a crystalline compound of cupreïne and hydroquinine is obtained, $C_{20}H_{26}N_2O_2,C_{19}H_{22}N_2O_2 + 2H_2O$. Hydroquinine forms similar compounds with conchinine and hydroconchinine. It also unites with two and with three molecules of cinchonidine, forming crystalline compounds which do not contain any water of crystallisation. Analogous compounds are formed with hydrocinchonidine and with homocinchonidine.

Anethoïlhydroquinine, $(C_{20}H_{26}N_2O_2)_2,C_{10}H_{12}O + 2H_2O$, is deposited in quadratic prisms from a solution of 5 parts of hydroquinine and 1 part of anethoïl in warm alcohol.

Hydroquinine forms three series of salts, which are as a rule more soluble than the corresponding salts of quinine. The normal sulphate, $(C_{20}H_{26}N_2O_2)_2,H_2SO_4 + 6H_2O$, has been previously described (*loc. cit.*). It forms a crystalline compound with phenol, $(C_{20}H_{26}N_2O_2)_2SO_3,C_6H_6O + 2H_2O$, which is sparingly soluble in cold water. The acid sulphate, $C_{20}H_{26}N_2O_2,SO_4H_2 + 3H_2O$, is freely soluble in water and alcohol. At 140°, the anhydrous salt is converted into hydroquinine sulphate. The disulphate is amorphous. Dichroic crystals resembling hydroquinine herepathite are obtained by adding potassium iodide (2 mols.) to an alcoholic solution of the acid sulphate (4 mols.), and acting on the product with an alcoholic solution of iodine.

Hydroquinine hyposulphite, $(C_{20}H_{26}N_2O_2)_2,H_2S_2O_2 + 2H_2O$, forms white prisms sparingly soluble in water. The *hydrochloride*,

$$C_{20}H_{26}N_2O_2HCl + 2H_2O,$$

crystallises in prisms, and is freely soluble in alcohol and water. The *platinochlorides*, $(C_{20}H_{26}N_2O_2)_2,H_2PtCl_6 + 3H_2O$ and $C_{20}H_{26}N_2O_2,H_2PtCl_6 + 2H_2O$, are amorphous and are sparingly soluble in water; the mercurochloride, $(C_{20}H_{26}N_2O_2HCl)_2HgCl_2$, crystallises in needles. The *hydrobromides*, $C_{20}H_{26}N_2O_2,HBr + 2H_2O$ and $C_{20}H_{26}N_2O_2,2HBr + 3H_2O$, also form needles. The neutral *hydriodide* is a colourless oily liquid which solidifies to an amorphous mass. Potassium iodide produces in acid solutions of hydroquinine salts a yellow, crystalline precipitate of the acid hydriodide, $C_{20}H_{26}N_2O_2,2HI + 4H_2O$. On the addition of iodine to the alcoholic solution of this salt, dichroic, needle-shaped crystals of the composition $C_{20}H_{26}N_2O,2(IH,I_2)$ are deposited. The *acetate*, $C_{20}H_{26}N_2O_2,C_2H_4O_2 + 5H_2O$, crystallises in needles and is freely soluble in alcohol and water. The *benzoate* and *salicylate* dissolve freely in alcohol. The benzoate is anhydrous. The *piperonate*, $C_{20}H_{26}N_2O_2,C_8H_6O_4$, is soluble in water and in chloroform. The *oxalate* is deposited from hot alcohol in prisms containing 6 mols. H_2O. The *tartrate* also crystallises in prisms containing 2 mols. H_2O. It is soluble in alcohol, water, and in a mixture of alcohol and chloroform. The *citrate* and *arsenate* crystallise with 10 mols. H_2O, the *phosphate* with 7 mols. H_2O. The *chromate*, $(C_{20}H_{26}N_2O_2)_2H_2CrO_4 + 6H_2O$, forms golden needles. The *dichromate* is an oily liquid.

Hydroquinicine dissolves freely in ether, alcohol, chloroform, and in dilute acids. The solution in dilute sulphuric acid is yellow; the colour changes to green on the addition of chlorine water and ammonia, but the mixture is not fluorescent. An ethereal solution of oxalic acid produces in an ethereal solution of hydroquinicine an amorphous precipitate soluble in chloroform. The normal sulphate crystallises in needles and dissolves freely in alcohol and in water.

Hydroquinine platinochloride, $C_{20}H_{26}N_2O_2,H_2PtCl_6 + H_2O$, forms orange-coloured crystals. Hydroquinine unites with methyl iodide, forming the compound $C_{20}H_{26}N_2O_2,MeI + C_2H_6O$. It crystallises in prisms of a yellow colour and dissolves in hot alcohol. It melts at 218°. On treatment with silver chloride, it is converted into the chloride $C_{20}H_{26}N_2O_2,MeCl + 2H_2O$. The acid *platinochloride*, $C_{20}H_{26}N_2O_2,Me{\cdot}HPtCl_6 + 2H_2O$, forms orange-coloured crystals, and the normal salt, $(C_{20}H_{26}N_2O_2Me)_2,PtCl_6$, pale-yellow needles. *Hydroquinine methylhydroxide* is amorphous. It is soluble in alcohol and water. The solutions are caustic and absorb carbonic anhydride.

Acetylhydroquinine, $C_{20}H_{25}N_2O_2Ac$, is amorphous. It melts at 40° and dissolves freely in alcohol, ether, benzene, and in acids. The solution is lævogyrate, and the solution in sulphuric acid is fluorescent. The *platinochloride* contains 2 mols. H_2O, and the normal sulphate, which is soluble in hot water and alcohol, crystallises with 9 mols. H_2O.

Hydroquinine is converted into hydrocupreïne dihydrochloride by the action of hydrochloric acid, sp. gr. 1·125, at 150°. *Hydrocupreïne*, $C_{19}H_{24}N_2O_2 + 2H_2O$, exists as a crystalline powder freely soluble in ether, alcohol, and chloroform. It melts at 168—170°, and exhibits a strong basic reaction and forms crystalline salts. Solutions of the normal salts have a greenish-yellow colour, the acid salts are colourless. The *sulphate*, $(C_{19}H_{24}N_2O_2)_2,H_2SO_4$, is sparingly soluble in water and in alcohol. The *tartrate* is sparingly soluble in water, but the dihydrochloride, $C_{19}H_{24}N_2O_2,2HCl + H_2O$, is freely soluble in water. The acid platinochloride, $C_{19}H_{24}N_2O_2,H_2PtCl_6$, is crystalline and insoluble in water.

Hydroquininesulphonic acid, $C_{20}H_{25}N_2O_2{\cdot}SO_3H + H_2O$, is prepared by dissolving hydroquinine in sulphuric acid at the ordinary temperature. The solution is poured into water and mixed with excess of ammonia. The acid crystallises in cubes and is soluble in boiling water, alcohol, and hot solutions of alkalis. It dissolves freely in acids, with which it forms crystalline compounds. The anhydrous acid melts at 239°.

The presence of hydroquinine in cinchona bark vitiates the results obtained in the estimation of quinine by the ordinary polariscopic method. W. C. W.

Apocinchine and Apochinine. By W. J. COMSTOCK and W. KOENIGS (*Ber.*, **20**, 2674—2689).—Analyses of salts and bromo-derivatives of apocinchine show that the formula previously assigned to the base (Abstr., 1882, 224) must be altered to $C_{19}H_{19}NO$; the formula ascribed to ethylapocinchinic acid (Abstr., 1885, 1248) is, however, retained. The authors now attribute the formation of the combustible, gaseous halogen compound (? methyl chloride) in the preparation of apocinchine to some secondary change in the reaction. *Apocinchine hydrobromide*, $C_{19}H_{19}NO,HBr$, crystallises from alcoholic hydrogen bromide in small, yellow needles, and melts at about 256°; the *hydriodide*, $C_{19}H_{19}NO,HI$, is a yellow, crystalline salt; the *platinochloride*, $(C_{19}H_{19}NO)_2,H_2PtCl_6$, forms orange-yellow crystals and melts at about 235°. The *acetyl*-derivative, $C_{19}H_{18}NOAc$, forms practically colourless crystals, and melts at 118—119°; the double phosphates of apocinchine and ammonium, barium, and potassium, were also prepared, and crystallise well.

Bromapocinchine, $C_{19}H_{18}NOBr$, is prepared by gradually adding bromine to apocinchine hydrobromide dissolved in equal parts of chloroform and acetic acid until the yellow perbromide begins to separate; sodium hydrogen sulphite is then added and the base obtained from the chloroform and aqueous layers by evaporation and precipitation. It is crystalline, melts at 186—188°, and is readily soluble in aqueous soda, benzene, chloroform, and ethyl acetate, less so in alcohol, carbon bisulphide, ether, and light petroleum. Bromapocinchine is not altered by prolonged boiling with alcoholic soda, and yields bromoform and cinchonic acid on oxidation with 4 per cent. chromic acid solution.

Dibromethylapocinchine, $C_{19}H_{16}NBr_2{\cdot}OEt$, is prepared by adding ethylapocinchine (10 grams) to well-cooled bromine (15 c.c.), digesting the product after 12 hours with sodium hydrogen sulphite, and extracting with alcoholic ammonia; the deposit from the alcoholic solution is then boiled with dilute sulphuric acid, the resulting solution treated with ether and aqueous soda, and the base obtained from the ethereal layer by evaporation. It melts at 116—118°. The alkaline solution, after separation from the ether, is found to contain dibromapocinchine.

Ethylapocinchinic acid forms a crystalline hydrochloride and hydrobromide. The *silver* salt, $C_{20}H_{18}NO_3Ag$, is a white, crystalline salt unaffected by light; the *platinochloride*, $(C_{20}H_{19}NO_3)_2,H_2PtCl_6$, is precipitated in voluminous, slender, straw-yellow needles, which are converted into small, compact, orange-yellow crystals, when the salt is heated on a water-bath for a short time.

Homapocinchine, $C_{17}H_{15}NO$, the compound formed together with carbonic anhydride and ethyl chloride when ethylapocinchinic acid is heated at 130° with hydrochloric acid (*loc. cit.*), crystallises from dilute alcohol in colourless crystals which contain water of crystallisation and melt at 184—185°. It is sparingly soluble in water, ether, benzene, and chloroform, readily soluble in hot alcohol, and differs from apocinchine, to which it shows much similarity, in its ready solubility in dilute aqueous soda. The *hydrobromide*, $C_{17}H_{15}NO_3HBr + H_2O$, crystallises in glistening, transparent, yellow needles or prisms, melts at 221—222°, and is sparingly soluble in water and in excess of dilute hydrobromic acid. The *ethyl*-derivative yields a crystalline, yellow sulphate. On fusion with potassium hydroxide, homapocinchine is converted into a compound which probably corresponds to oxyapocinchine. When oxidised in very dilute solution with permanganate, ethylapocinchine yields a mixture of solid acids which dissolve in dilute sulphuric acid and alkalis. Ethylapocinchinic acid is one constituent of the mixture. To effect a separation, the product is boiled with hydrobromic acid (sp. gr. 1·49), and the solution treated with aqueous soda which precipitates homapocinchine; careful acidification of the filtrate then precipitates a mixture of at least two acids, of which the one of lower melting point is the more soluble in alcohol. The more soluble acid, $C_{18}H_{13}NO_4$ or $C_{19}H_{15}NO_4$, dissolves in dilute mineral acids, melts at 230° with the evolution of gas, and at 240° yields carbonic anhydride and a compound, $C_{17}H_{13}NO_2$. This crystallises from dilute alcohol in colourless, silky needles, melts at 223°, is not volatile without decomposition, and is soluble in dilute acids and alkalis. The hydrobromide, sulphate, and nitrate are crystalline, and sparingly soluble.

Acetyloxyapocinchine, $C_{19}H_{18}NO_2Ac$, melts at 201—203°, and is soluble in alcohol, benzene, and light petroleum.

From considerations based on analyses of its salts, the authors have adopted the formula $C_{19}H_{19}NO_2$ for chinine, instead of that previously proposed (Abstr., 1885, 910). *Chinine hydrobromide*, $C_{19}H_{19}NO_2,HBr$, crystallises in long, sulphur-yellow needles, and is decomposed by water.

The remainder of the paper is devoted to a discussion of the constitution of these alkaloïds, in which the authors adhere to the views already put forward with regard to apocinchine (Abstr., 1885, 1248; 1887, 600), and suggest that cinchine may possibly be a dialkylamidophenylquinoline, and that the second benzene nucleus is present in a partially hydrogenated form. W. P. W.

Strychninesulphonic Acids. By C. Stoehr (*Ber.*, **20**, 2733—2734).—A note calling attention to the fact that the results obtained by Guareschi (Abstr., 1887, 853) are essentially the same as those previously arrived at by the author (Abstr., 1886, 269). W. P. W.

Peculiar Modification of Urobilin. By E. Salkowsky (*Chem. Centr.*, **18**, 1089).—On examination of a sample of urine peculiarly rich in urobilin, it was observed that on keeping this colouring matter disappeared without any marked change of the colour of the urine. This conversion of the urobilin seems not to be conditioned by the ammoniacal fermentation of the urine or by the presence of micro-organisms. Urobilin is a substance readily decomposed, and passes into a modification which, although still coloured, shows no absorption-bands, nor fluorescence with zinc chloride in ammoniacal solution, and is not taken up by chloroform. It is probable that in most normal urines, urobilin, as well as its decomposition-products, is present. V. H. V.

Chemical Formation of Albumin. By C. F. W. Krukenberg (*Chem. Centr.*, 1887, 1085).—When keratin, previously purified by the action of pepsin and trypsin, is heated with water in a sealed tube, it dissolves to form an alkaline liquid, possessing a strong odour of hydrogen sulphide. This liquid contains a non-dialysable substance, keratinose, precipitated by ammonium sulphate, which agrees with hemialbumose as regards these reactions, although it does not give the hydrochloric acid test. Keratinose is converted by pepsin and hydrochloric acid at a blood-heat into keratinpeptone, which is not precipitated by ammonium sulphate. Under the same conditions spongin yields *spongionose*, a soluble, indiffusible substance; this is also converted into spongiopeptone. By the decomposition of spongin, carbamide seems to be formed. The author considers that the albuminoïds and skeletins are related to albumin as methyl to methyl ether. V. H. V.

Coagulation of Albumin. By V. Michailoff (*Chem. Centr.*, 1887, 1088).—According to the author the coagulation of albumin is due to one of two phenomena, namely, the true coagulation induced by the action of ferments or heat, a process analogous to etherification or the formation of polyhydro-silicates or glycols, and a pseudo-coagulation caused by a loss of "gelatinose-water," which corresponds with the loss of water of crystallisation of salts. The coagulating power of salts on solutions of albumin is dependent on the nature of the acid and base therein contained; the maximum effect is produced by ammonium, the mean by sodium, and the minimum by potassium salts. Again, in the case of ammonium salts, the sulphate is more efficient than the nitrate, and of potassium salts the sulphate than the chloride. V. H. V.

Egg Albumin and Albumoses. By R. H. Chittenden and P. R. Bolton (*Studies from Lab. Physiol. Chem., Yale Univ.*, 2, 126—155). —These experiments were designed to contrast the products of digestion of egg albumin with those obtained by Kühne and Chittenden from fibrin. Four samples of albumin were prepared; in some cases it was separated from globulin by saturation with magnesium sulphate, in others by dilution and the subsequent addition of acetic acid. An elementary analysis of these four samples gave the following average percentages:—C, 52·18; H, 6·93; N, 15·81; S, 1·87; O, 23·21. Further, coagulated products did not differ in composition from non-coagulated albumin. These results do not agree with any of the formulæ ascribed to albumin by previous observers.

Peptic digestion of the albumin resulted in the formation of albuminoses of which the percentage composition and reactions were determined. In composition they were found to differ from each other somewhat more than the albumoses from fibrin; collectively, however, there is less difference in composition between the albumoses and the egg albumin from which they were formed than in the case of the albumoses from fibrin. The following table gives the final results:—

	Fibrin products.			Egg albumin products.		
	Proto-albumose.	Deutero-albumose.	Fibrin.	Proto-albumose.	Deutero-albumose.	Egg albumin.
C........	50·77	50·65	52·68	51·07	51·62	52·33
H........	6·78	6·83	6·83	6·98	6·97	6·98
N........	17·14	17·17	16·91	16·00	15·82	15·85
S........	1·08	0·97	1·10	1·95	1·96	1·82
O........	24·23	24·38	22·48	24·00	23·63	23·02

In their reactions the different albumoses (proto-, deutero-, hetero-, and dys-albumose) obtained from egg albumin do not differ essentially from those obtained from fibrin. W. D. H.

Metallic Compounds of Albumin and Myosin. By R. H. Chittenden and H. H. Whitehouse (*Studies from Lab. Physiol. Chem., Yale Univ.*, 95—125).—Many researches on the subject of the metallic compounds of albumin have been carried out since Lieberkühn attempted to establish the molecular weight of albumin by the analysis of copper albuminate. The more recent work of Harnack (Abstr., 1882, 747) showed that two compounds of albumin (from white of egg) with copper occur, one containing 1·35 per cent., and the other 2·64 per cent. of copper. In the present research, albumin was freed from globulin by the use of dilute acetic acid, and both the acetate and sulphate of copper were used in the preparation of the albuminate. The precipitate was well washed with water, powdered, and dried. The percentage of copper was first determined as cupric oxide by ignition and weighing: the oxide was then dissolved in dilute nitric acid, treated with hydrogen sulphide, and the amount of cuprous sulphide obtained weighed. By the former method, in 15 preparations the average result was 1·17 per cent. of copper; and by the latter method 0·94 per cent.; the preparations, therefore, contain 0·23 per cent. of ash. In order to obtain less ash, Harnack dissolved the albuminate in sodium carbonate and reprecipitated it by the careful addition of acid; this process was repeated several times. This treatment certainly increases the percentage of copper, but is a source of error, as the sodium carbonate withdraws a portion of the albumin. Long-continued washing with water also causes partial dissociation of the compound. The results obtained correspond with the formula $(C_{72}H_{112}N_{18}SO_{22})_4 + Cu - H_2$.

A normal lead salt causes a small precipitate when added to albumin, whilst with basic lead acetate the albumin is completely precipitated. This confirms the previous statement of Berzelius (*Lehrbuch der Chemie*, **9**, 29). The preparations were well washed from both lead and albumin, dried, and the lead was determined, first by simple ignition, and then obtained as sulphate, which was ignited. The results indicate that more than one compound of lead is formed, that made by the addition of a large excess of the basic acetate, containing about five times as much lead as the ordinary basic lead compounds. An iron compound which was found to be more stable than the copper albuminate, and corresponded fairly well with the formula $(C_{72}H_{112}N_{18}SO_{22})_4 + Fe - H_3$, and a zinc compound, $(C_{72}H_{112}N_{18}SO_{22})_4 + Zn - H_2$; acid compounds with uranium, $(C_{72}H_{112}N_{18}SO_{22})_3 + U - H_2$; with mercury, $(C_{72}H_{112}N_{18}SO_{22})_4 + Hg - H_2$; and with silver, $(C_{72}H_{112}N_{18}SO_{22})_2 + Ag_2 - H_2$, were also prepared and analysed. Much stress is not laid on such formulæ, as it seems possible to form a large variety of compounds by simply modifying the conditions of precipitations. This, with the undoubted tendency of the compounds to dissociation, may account for the lack of agreement in the results of different workers. Similar compounds prepared from myosin obtained by extracting ox flesh with 15 per cent. ammonium chloride were prepared, and the percentage results show that these two forms of proteïd matter do not form corresponding compounds with the metallic salts used. This is illustrated by the following table:—

	Egg albumin.	Myosin.
Copper compound	0·94 per cent. Cu	1·17 per cent. Cu
Iron ,,	0·95 ,, Fe	2·29 ,, Fe
Zinc ,,	0·91 ,, Zn	0·72 ,, Zn
Uranyl ,,	4·60 ,, U	7·49 ,, U
Mercury ,,	2·89 ,, Hg	2·43 ,, Hg
Lead ,,	2·56 ,, Pb	—
Silver ,,	4·09 ,, Ag	—
Nickel ,,	—	4·70 ,, Ni
Cobalt ,,	—	6·03 ,, Co

W. D. H.

Caseïn and Caseoses. By R. H. CHITTENDEN and H. M. PAINTER (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 156—199).—Danilewsky (*Zeit. physiol. Chem.*, **7**, 433) has asserted that caseïn is a mixture of two proteïds, caseoprotalbin, partially soluble, and caseoalbumin, insoluble in hot 50 per cent. alcohol. Hammarsten (*ibid.*, **7**, 227) has shown that the peculiar behaviour of Danilewsky's caseïn is due to its containing calcium phosphate, the presence of which impurity depends on the use of hydrochloric acid in the precipitation of the caseïn, as this acid does not favour the removal of the salt as well as acetic acid. He also considers that caseïn is a single proteïd. In the present research, seven distinct preparations of caseïn were made. Elementary analyses show a close agreement throughout, and the results moreover accord closely with those of Hammarsten.

In the digestion of caseïn with hydrochloric acid, peptones are ultimately formed, and the name caseose is given to the intermediate products. These were separated by the methods of Kühne and Chittenden into proto-, hetero-, and deutero-caseose, which correspond with the albumoses with similar names. The quantity of heterocaseose obtained was usually very small. The reactions characteristic of albumoses apply generally to the caseoses. Unlike proto-albumose however, *protocaseose* is precipitated from aqueous solutions by acetic acid. The average of the analyses of 10 preparations of protocaseose gives the following percentage results:—

	C.	H.	N.	S.	O.
Protocaseose	52·89	7·10	15·94	0·95	23·12
Caseïn	53·30	7·07	15·91	0·82	22·08

Deuterocaseose contains a smaller percentage of carbon than protocaseose, and *heterocaseose* contains fully as much carbon as caseïn itself.

An insoluble, semi-gelatinous substance which separates in the first stage digestion has not yet been investigated. Weyl's commercial "caseïn-peptone" contains large quantities of caseoses.

W. D. H.

Animal Tannin. By M. VILLON (*Chem. News*, **56**, 175).—Corn weevils (*Calandra granaria*) were killed, ground in a mortar, and digested for one hour in boiling 90 per cent. alcohol. The residue from the evaporation of the extract is taken up with ethyl acetate at 50°, and precipitated by means of ammoniacal zinc acetate. The precipitate is decomposed with oxalic acid, and the solution evaporated in a vacuum. In this way 3 per cent. of a substance having all the general properties of tannin is obtained from the weevils. This animal tannin, *fracticornitannin*, forms small reddish-yellow scales.

D. A. L.

Physiological Chemistry.

Influence of some Organic and Inorganic Substances on Gas Metabolism. By R. H. CHITTENDEN and G. W. CUMMINS (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 200—236).—The question investigated was the consumption of oxygen and the elimination of carbonic anhydride. The animal, a rabbit, was confined in a large bell-jar, through which air was drawn by means of three aspirators, which were arranged to work evenly, and emptied themselves in half an hour. Two-fifths of the mixed air was drawn successively through three absorption-tubes, each of which contained 100 c.c. of standard baryta. The carbonic anhydride was estimated by titration with standard oxalic acid. The results obtained are not absolute, but express quite well the comparative action of the various substances experimented with. It was found necessary to have the animal in a state of hunger during an experiment. Accordingly it was deprived of food for three days previous to the experiment, as well as during the three days for which the experiment lasted. During the last two of the three days, the substance experimented with was given in small and oft-repeated doses. Every day numerous determinations of carbonic anhydride were made, and comparison could then be made between the normal excretion of that substance and that during the administration of the drug. Observations were also made on the body temperature. The following are briefly the results obtained with the following substances:—Uranyl nitrate acts slowly, but when taken in sufficient quantity tends to raise materially the body temperature, and increase very noticeably the excretion of carbonic anhydride. Copper sulphate shows a marked influence in depressing body temperature, and a still greater influence in diminishing the production of carbonic anhydride. Arsenious oxide given in non-toxic doses also diminishes the excretion of carbonic anhydride, presumably through its action on the metabolic activity of the tissue cells. Tartar emetic acts similarly. Morphine sulphate has but little action; a slight fall in the excretion of carbonic anhydride immediately after a dose must be attributed to the semi-somnolent condition of the animal. Quinine sulphate, which is so important as an antipyretic, is found in a healthy hungry rabbit to have only a very slight depressing influence on body temperature, and a minimum effect on the production of carbonic anhydride. Cinchonidine sulphate produced a slight rise of temperature and a gradual diminution in the amount of carbonic anhydride excreted; it also caused tetanic convulsions and finally death. Antipyrine had little effect, the only change being a fall in temperature just before death. W. D. H.

Action of Uranium Salts on Digestive Ferments. By R. H. Chittenden and M. T. Hutchinson (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 55—67).—Very small quantities of uranium salts promote the activity of saliva; larger amounts hinder and finally stop its amylolytic action. 100 c.c. of digestive mixture contained 2 c.c. of neutralised saliva, and 1 gram of pure potato-starch. The mixture was warmed at 40° for 30 minutes and then boiled to prevent further action; the amount of sugar present was estimated as dextrose by Fehling's solution. This was compared with other digestive mixtures to which a certain percentage of a uranium salt was added. The following table illustrates the results obtained with uranyl nitrate:—

Amount of salt added.	Total amount of reducing substances.	Starch converted.	Relative amylolytic action.
0·000 per cent.	0·4135 gram.	37·21 per cent.	100·0
0·001 "	0·4083 "	36·74 "	98·7
0·003 "	0·3873 "	34·85 "	93·6
0·005 "	0·3698 "	33·28 "	89·4
0·001 "	0·3612 "	32·50 "	87·3
0·003 "	0·3131 "	28·17 "	75·5
0·008 "	trace	—	—

Uranyl acetate was more inhibitory in its action, due possibly to its greater acidity; 0·0003 per cent. increases, 0·003 per cent. stops amylolytic action. Experiments with similar results were obtained with ammonio-uranous sulphate, sodio-uranic sulphate, potassio-uranic oxychloride, and ammonio-uranic citrate. The action of the salts varies with different specimens of saliva, according to the amount of proteïd present which is precipitated by them. Loss of amylolytic power is due in part to partial direct destruction of the ferment as well as to change in reaction of the fluid. There must, however, be something in addition to the mere presence of these salts dependent on chemical constitution that controls the action of the ferment.

The same salts were also investigated in regard to their action on the proteolytic action of pepsin-hydrochloric acid. Similar series of experiments were made, and the results compared by estimating the amount of fibrin left undigested after an hour's action. The potassium uranic oxychloride was the only salt that produced initial stimulating action on the ferment; the others all retarded its activity. The difference in action of the various salts seems to depend on the acid liberated from them; the acids which are not capable of working with pepsin will most readily retard gastric digestion; thus the acetate retards digestion more than the nitrate; acetic acid mixed with pepsin is practically inactive, whilst nitric acid is about four-fifths as active as hydrochloric acid.

A similar series of experiments showed that uranium salts also retarded the action of the pancreatic ferment. W. D. H.

Digestion in Rhizopods. By M. GREENWOOD (*Journ. of Physiol.*, **8**, 263—287).—The authoress has continued her observations on the digestive processes in *Amœba* and *Actinosphærium* (Abstr., 1886, 1053) with the following results: (1.) The ingestion of solid matter is promiscuous in amœba, that is nutritious and innutritious matters are taken in with equal readiness. Actinosphærium, on the other hand, rarely ingests innutritious particles. (2.) The act of ingestion in amœba is accompanied by the emission of pseudopodia; in actinosphærium these may or may not be thrown out. (3.) The nutritious matter taken in by amœba is not surrounded by fluid when it lies in the endosac. (4.) Nutritious particles are in both animals digested by fluid poured out around them. This fluid has no action on the cuticle of organisms, or on cellulose or siliceous cell-walls. Fat and starch are apparently not digested by it. It is a colourless fluid, which acts on coagulated, and still more so on non-coagulated proteïd matter. It has no action on litmus or carmine particles, accidentally enclosed with nuritious particles, and is therefore neutral in reaction. (5.) The secretion is more active in actinosphærium than in amœba. (6.) Chlorophyll is changed to a dark-brown colour by amœba; this is not so marked in actinosphærium. (7.) Ejection is performed at the hind end of amœba, either by means of a vacuole, or often in the case of algæ without one. An excretory vacuole is always present in actinosphærium. (8) The time between ingestion and ejection is difficult to determine, and varies with the size and digestibility of the ingesta; it averages 3 to 4 days in amœba. In actinosphærium the digestive act is shorter and occupies from 1½ to 8 hours. W. D. H.

Dehydration of Glucose in the Stomach and Intestines. By R. H. CHITTENDEN (*Studies from Lab. Physiol Chem., Yale Univ.*, **2**, 46—53).—Pavy (*Chem. News*, **49**, 128, 140, 155, 162, 172, 183) brought forward evidence to show that there exists, particularly in the stomach and intestines of rabbits, a ferment which has a dehydrating action on glucose, transforming it into a substance with less cupric oxide reducing power, akin to maltose. This substance is formed at a temperature of 48° by bringing a solution of glucose into contact with the stomach and intestines of a rabbit; by boiling it with dilute sulphuric acid, it is again converted into glucose. In the present research these experiments were repeated, but gave an entirely negative result, rabbits and cats being the animals used, in different stages of digestion. Ogata (*Jahrsber. für Thierchem.*, **15**, 275) has also been unable to confirm Pavy's results. W. D. H.

Influence of Antimonious Oxide on Metabolism. By R. H. Chittenden and J. A. Blake (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 87—94).—Antimonious oxide was used instead of tartar emetic, because of its probable slower toxic action, and also because it has been so extensively used as a means to induce or to aid in the production of fatty degeneration, for instance, in the production of fatty livers in geese (H. C. Wood, *Therapeutics*, 161).

The nitrogen, phosphorus, sulphur, and chlorine were estimated daily in the urine of a dog, to whom a fixed diet was administered, first for a period without and afterwards for a period with the addition of small quantities of antimonious oxide. The results of the two series may be stated as follows:—

Daily Average of Constituents of Urine in grams.

	Nitrogen.	Phosphorus.	Sulphur.	Chlorine.
1. Without antimony....	11·743	0·7251	0·6708	0·5592
2. With antimony	12·028	0·7292	0·6534	0·5070

The conclusion is drawn that small repeated doses of antimonious oxide are without influence on the excretion of nitrogen, sulphur, and phosphorus, and that consequently this compound, at least when taken in non-toxic doses, has no action on proteïd metabolism.

W. D. H.

Asparagine as a Nourishing Constituent of Food. By H. Weiske (*Landw. Versuchs-Stat.*, **34**, 303—310).—A review of the work done by various chemists. It is shown that the mass of evidence produced is in favour of asparagine being a nutrient for herbivora, and that under appropriate conditions it prevents waste, and causes the formation of albumin. As to its influence on omnivora and carnivora, this does appear to be the case, but on the contrary it produces strong diuretic action, and destruction of albumin; however, more experiments are necessary for the complete elucidation of the problem.

E. W. P.

Ash in Bones of Different Ages. By W. P. Mason (*Chem. News*, **56**, 157—159).—The author has examined for ash and as to brittleness several samples of bones, both from males and females, from bodies recently dead and from living people (amputations). In all cases the history of the bone was known, and the ash determined in portions selected from the dense portion of the middle of the shaft of the femur. All diseased bones, or bones from persons suffering from ailments affecting the bones, were excluded. His results show that from manhood to old age, there is no variation in the amount of ash in bones. That the brittleness of old bones is due to the material rather than the structure; that it is not therefore due to the increase of spongy tissue and diminution of the denser portions of the bone as age advances (Frémy's supposition); nor does it arise from the increase in the percentage of inorganic salts.

D. A. L.

Distribution of Antimony in the Organs and Tissues. By R. H. Chittenden and J. A. Blake (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 68—86).—These experiments were undertaken in order that data of medico-legal importance might be obtained; the relative distribution of the poison in the tissues giving indications of the length of time that intervenes between the administration of the poison and death. The only trustworthy method of estimating small quantities of antimony was found to be the electrolytic method (Classen, Abstr. 1885, 191, 932); preliminary experiments were performed which showed that this method acts well when antimony is mixed with organic matter, and also in urine. A feeble current was used and allowed to act for many hours; the antimony was collected at the negative pole which was a platinum capsule. When the separation of the metal was complete, it was found necessary to remove all organic matter by washing with water before breaking the current, otherwise the antimony quickly redissolved.

Tables are given of the results in which various compounds of antimony were given by hypodermic injection, by the mouth, and by the rectum in dogs and rabbits. The brain and liver were the organs in which the metal tends most to accumulate, although if sufficient time elapses between the giving of the poison and death, it tends to spread more uniformly through the body; the more soluble compounds of antimony like tartar emetic produce their effects more rapidly than the insoluble forms like antimonious oxide.

W. D. H.

Formation and Elimination of a Ferruginous Pigment in Poisoning with Toluylenediamine. By Engel and Kiener (*Compt. rend.*, **105**, 465—467).—In acute cases which end in death in a few hours, there is no icteria and no hæmoglobinuria, but the victim falls into a state of coma and dies. There is intense congestion of all the organs and especially of the lungs, but the spleen and marrow contain no excess of pigment.

When death ensues after a few days, there is always icteria and often hæmoglobinuria, and the urine is loaded with fat and yellow and brown pigment granules which are variable in composition but sometimes contain iron. The ferruginous pigment formed by the destruction of the hæmoglobin accumulates in the spleen and marrow. It seems to be formed from the hæmoglobin in the protoplasm from the cellules and not from the red corpuscles. The deposits in the liver are less constant and more local.

In chronic cases ending in death after several weeks, the icteria is moderated and is often retarded for a long time. There is no hæmoglobinuria and no granular pigment in the urine. The animal eventually succumbs to anæmia, which is followed by coma, and after death the spleen, marrow, and liver contain a greater quantity of the ferruginous pigment than in acute cases, and there is a notable quantity in the kidneys and in the lymphatic ganglions of the abdomen.

C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Nitrites during Nitrification of Ammoniacal Solutions. By J. M. H. MUNRO (*Chem. News*, **56**, 62—64).—Gayon and Dupetit have suggested that the nitrite formed during nitrification is produced by reduction of previously formed nitrate; they suppose the nitrifying organism either to acquire reducing powers by living at the bottom of a solution, or else that it is not pure but mixed with denitrifying bacteria, and that the nitrate reduced by one or other of these, supplies oxygen for the oxidation of organic matter present in the solution. The present experiments disprove this and show (1) that a solution of potassium nitrate, seeded with soil from a recently nitrified solution, develops no nitrite even though kept for a year in a stoppered bottle; (2) that a solution of ammonium chloride, seeded with the same soil, and with no other added organic matter, formed nitrite in increasing quantities from the third day to the 139th, when almost all the ammoniacal nitrogen was present in that form, afterwards passing into nitrate; (3) that a solution containing both potassium nitrate and ammonium chloride ($3KNO_3 + NH_4Cl$) seeded with the same soil, ran through exactly the same course as the preceding. If an organism were present capable of reducing nitrate to nitrite with simultaneous oxidation of ammonia to nitrite, four times the quantity of nitrite produced in the preceding case could theoretically be formed: instead of this, the amounts were almost exactly equal, and both a little under that corresponding to the whole of the ammoniacal nitrogen. The author concludes that the nitrite is formed by oxidation of the ammonia.
J. M. H. M.

Chemical Nature of Aristolochia Serpentaria. By M. SPICA (*Gazzetta*, **17**, 313—316).—The *Aristolochia serpentaria* (Virginia snake-root) grows in the southern part of North America, especially in the mountainous districts of Carolina and Virginia; various preparations of its roots are used medicinally as febrifuges. Its chemical nature has previously been examined by Buchholz, Chevallier, and others, who have obtained besides other products a volatile oil. On distilling the ethereal extract of the root in a current of steam, a yellowish-green oil is obtained, heavier than water, and having an odour resembling that of camphor and valerian. This oil, after treatment with potash, is cooled by a freezing mixture, which causes the separation of a crystalline stearoptene; this melts at 198°, boils at 212°, and is shown by chemical analysis and its physical properties to be borneol. No very definite product could be obtained from the oil from which the borneol had thus been separated.
V. H. V.

Constituents of Scopolia Root. By H. HENSCHKE (*Chem. Centr.*, 1887, 1087—1088).—*Scopolia japonica*, or Japanese belladonna, is a species of Solanaceæ indigenous to Japan and China. Two alkaloïds are manufactured commercially from its roots, namely, scopoleïne and rotoïne, and Eijkman has obtained two substances, a glucoside, scopolin, and scopoletin, its decomposition product. It is here shown that the root of the plant contains no peculiar alkaloïd, but the three mydriatic alkaloïds, atropine, hyoscyamine, and hyoscine in variable proportions.

Commercial rotoïne is not a distinct base, but a mixture of the sodium salts of fatty acids of high molecular weight. The fluorescent substance, scopoletin, obtained by Eijkmann, is identical with the so-called chrysatropic acid of Kunz, whilst it is further probable that it is identical with methylæsculetin. V. H. V.

Oil of Lallemantia Iberica. By L. RICHTER (*Landw. Versuchs-Stat.*, **34**, 383—390).—The oil expressed from the seeds of *Lallemantia iberica* (Fisch et May) has the property of being the most rapidly "drying" of all known oils. The ethereal extract of the seeds may be completely decolorised by animal charcoal, and on evaporation of the ether, a pale-yellow oil is obtainable which after some time becomes slightly opaque; the opacity may be removed by filtration, when a clear fat of faint but acrid odour, whose taste resembles that of linseed oil, is left on the filter. The oil is insoluble in cold, but readily soluble in hot alcohol, insoluble in cold acetic acid (1·0643). The sp. gr. of the oil is 0·9336 at 20°, and its solidifying point −35°; the free fatty acids melt at 22·2°, and resolidify at 11·0°. When exposed to the air for five days, a crust is formed at the edge of the liquid, but complete resinification, or "drying," occurs in 24 hours, after it has been heated at 150° for three hours. Casselman states that complete drying of linseed oil only occurs after 36 to 48 hours' heating at 150°; poppy oil requires four to five days, and hemp oil still longer.

It behaves towards nascent nitrous acid in the same manner as linseed oil, a dark-red doughy mass being produced. Mixed with concentrated sulphuric acid, the temperature rises to 102° and even to 120°.

According to v. Hübl's method, the oil purified from fat, unites with 162·1 grams of iodine per 100 grams oil, whilst the fat combines with 166·7 grams of iodine. No other oil approaches closely to this figure except linseed. As the absorption of iodine by the oil corresponds with its facility for drying, it was necessary to estimate the amount of oxygen absorbable; this was done by Livache's process, when it was found that the oil absorbed 15·81 per cent. of oxygen in one day, whilst the fatty acid absorbed 16·58 per cent. in 28 days; linseed absorbs 14·3 per cent. in two days, and its fatty acid 11 per cent. in eight days. Hehner's and West-Knight's methods for determining the percentage of insoluble fatty acids in the oil were both used, the former method showed the presence of 93·3 per cent., and the latter 94 per cent., and the volatile oil (Reichert's method) amounted to 1·55. The figures representing saponifiability (Köttstorfer) were 184·9 (milligrams KHO), and 9·75 per cent. of glycerol was found, corresponding with

99·74 per cent. of glycerides. The lead salt was used to cause separation of the liquid and solid fatty acids, when it was found that of the latter there was 6·55 per cent. and of the former 93·45 per cent. present.

The quantitative reactions are given in the original.

When grown as a field crop, Lallemantia yielded 2031 kilos. seed and 6314 kilos. straw per hectare. E. W. P.

Are Nitrates indispensable for the Growth of Field Crops? By O. Pitsch (*Landw. Versuchs-Stat.*, **34**, 217—258).—The carefully conducted experiments for the elucidation of the above question appear to be most satisfactory, and the decision arrived at is that at any rate barley, oats, beans, and wheat can and do grow in a soil absolutely destitute of nitrates, free from all nitrifying bacteria, but in which nitrogenous manures are present as ammonium sulphate. The experiments were made during two seasons, and all the precautions taken, the progress of the various plants grown, and the apparatus employed are fully detailed. In outline, a rich soil was first heated in an oil-bath to destroy all bacteria, then thoroughly washed by upward displacement, to free it from all nitrates, again heated and then placed, the first year, in large beaker glasses, and in the second season in iron vessels 62 cm. × 25 cm.; the seeds were sown, and a thick covering of cotton wool placed on the surface of the soil in a suitable holder of wire net, so as to prevent access of all aerial spores; distilled water was used for watering by a special method described in full, whereby the water was admitted from below. Two sets of such vessels and seeds were employed. To the soils used in the first year, bicalcium potassium phosphates and ammonium sulphate were added, both to the original and to the parallel sets, the difference between the two being that the soil of the parallel sets was neither heated nor covered over with cotton wool. In the second year, however, the soil underwent the same process in both sets, but in place of ammonium sulphate being added to the controlling sets, sodium nitrate was added, and no cotton wool used. The results in both years were, however, similar, namely, that the growth of the plants under such peculiar conditions as total absence of nitrates was not largely affected—certainly there was a difference, but not at all remarkable; the plants were able to grow healthily, but perhaps not robustly without any nitrates. It was noticed that those plants which could obtain no nitrates, but had to be content with nitrogen in other forms, came to a standstill for a short time early in their growth, and after a short period of rest, again grew normally. The author tried to account for this in the first year, by the fact that as the manure had not been mixed thoroughly with the soil throughout its whole depth, the lower roots were unable to obtain nitrogen, consequently no growth was made until new roots were formed higher up, but after the experiments of the second season had been made, he was obliged to abandon this theory, for although he had mixed the manure thoroughly with the soil, yet this arrest of growth again occurred, whilst no such effect was produced in the soil containing nitrates. E. W. P.

Agricultural Experiments. By J. RAULIN (*Compt. rend.*, **105**, 411—414).—In order to avoid, in agricultural experiments, errors due to differences between the natural fertility of contiguous patches of soil, the experimental plot should be divided into three rectangular sections, A, B, and C, which are treated separately. As a rule, the results with A and C differ, and in a few cases the differences are quite irregular. Usually, however, the fertility of the plot varies gradually, so that the mean of A and C is practically identical with B.

Experiments made in this way show that superphosphates and precipitated calcium phosphate produce a distinct increase in the wheat crop, whilst with fossil phosphates and with slags the results are doubtful, the apparent increase not being greater than the variations between the three sections of the plot. C. H. B.

Analytical Chemistry.

Grinding Mill for Minerals. By K. ZULKOWSKY (*Ber.*, **20**, 2664—2669).—A description of a mill in which minerals may be readily reduced to fine powder. The grinding surfaces are of agate, and the pestle is so arranged that it can be rotated by a water-motor against the lower surface with a pressure capable of being varied at will. The material, already reduced to the coarseness of sand, is introduced into the mill through a sector cut in the pestle.

W. P. W.

Determination of Sulphur in Pyrites. By J. W. WESTMORELAND (*J. Soc. Chem. Ind.*, **6**, 84—87).—It is shown that the results obtained by Lunge's "old process" (precipitation of the sulphur from ferric solutions), agree closely with those given by the new process (precipitation after separation of the ferric oxide by ammonia), which is therefore a needless elaboration. The new method is also liable to losses caused by an extra filtration and washing, and by sulphur retained in the ferric oxide, whilst sulphur is liable to be introduced by the ammonia and hydrochloric acid employed. The results obtained by Lunge's processes express the total percentage of sulphur in Spanish pyrites; it is, however, necessary to use only a moderate excess of barium chloride for precipitation, great care being taken in the use of hydrochloric acid when washing this precipitate.

D. B.

Estimation of Sulphur in Pyrites. By G. LUNGE (*J. Soc. Chem. Ind.*, **6**, 96).—The author criticises Welch's process (Abstr., 1887, 180) for assaying iron pyrites for sulphur available for sulphuric acid manufacture, and shows that the experiments having been made with impure lead sulphide are not conclusive. D. B.

Kjeldahl's Method of Estimating Nitrogen. By F. W. DAFERT (*Landw. Versuchs-Stat.*, **34**, 311—353).—In this article, are detailed in full the results of experiments made for the purpose of testing the value of Kjeldahl's process for estimating organic nitrogen, and of an examination of the various modifications of this process, as recommended by Kreusler and others.

Estimation by the Original Process.—Certain nitrogenous compounds only seem to yield their nitrogen in the ammoniacal forms, the result being that the process is inaccurate with regard to others; of the latter class, anilines and hydrazines are special examples, but some compounds, contrary to expectation, yield their nitrogen as ammonia more readily than others; as for instance, it was expected that hydrazines would yield ammonia more completely and quickly than nitro-compounds, but the contrary is the case.

The Action of the Sulphuric Acid.—To aid the solution of this question, Kreusler's modification, where phosphoric anhydride is added to the sulphuric acid, was employed; sugar was also added. The explanation which is given is, that the sulphuric acid removes from the substance the elements of water and of ammonia, and the sulphurous anhydride formed in the reaction reduces the nitrogenous compound; the addition of organic matter (sugar) to the nitrogenous compound slackens the formation of ammonia when the compound is not volatilised by the acid; consequently to obtain quantitative results, the sulphuric acid must not volatilise the compound, nor completely decompose it, for the analysis of some substances by this method free nitrogen accompanies the ammonia.

The Action of Permanganate.—The presence of the permanganate when used in company with the mixture of acids, causes a destruction of the organic matter present, the nitrogen being so separated that nearly the whole of it is transformed into ammonia; as a rule this modification of Kjeldahl's process may be employed for all quantitative analyses, but it is necessary that the mixture shall be thoroughly and sufficiently heated.

The Addition of Metallic Salts.—This modification of Wilfarth's renders the original process more rapid, although the time required for the analysis is shortened very considerably by the addition of mercury, it is at the cost of accuracy; it should only be introduced in those cases where very stable compounds are under examination, or also when the compounds readily give up their nitrogen as ammonia. From careful examination, it appears that the discrepancies which exist between the results obtained by Kjeldahl's original method, Wilfarth's and Ulsch's (addition of platinum chloride), are due to loss of nitrogen as nitrogen, and not to an insufficiency of heating, when the compound is only slightly stable. The author considers that Wilfarth's explanation of the reaction which occurs when metallic salts are present, is satisfactory, but he also adds that when those compounds which do not resist the action of sulphuric acid well, or which are readily oxidised, are dealt with, the addition of the metallic salt causing violent oxidation, ammonia may be in part replaced by nitrogen; increasing the quantity of platinum, addition of oxygen and mixing with organic substances may also result in loss, even when the compound is not easily decomposed. Mercury should be always employed when very stable compounds are to be analysed; amines and alkaloïds resist oxidation, but Ulsch's process must not be used because of its uncertainty, except in special cases, for example, with potassium nitrate.

General Application.—Nitrogenous compounds may be divided into two classes as regards the applicability to them of Kjeldahl's process of analysis. In the first are placed those which can be analysed without any previous treatment, for example, all amides and ammonium bases, pyrroline and quinoline compounds, alkaloïds, bitter substances, albuminoïds and their allies, and perhaps the indole group; whilst to the second class belong all nitro-, nitroso-, azo-, diazo-, hydrazo-, and azoamido-compounds, nitrates and nitrites, the hydrazines, and possibly the cyano-compounds. Two methods may be employed for the previous treatment of this second class: addition of an organic substance, or reduction with zinc-dust, and even the two combined, but the choice of which is to be used must rest with the analyst. This uncertainty will for the present preclude Kjeldahl's process, or its improvements, from supplanting Dumas's older and exact method. For the estimation of nitro-compounds, it is recommended to dissolve the substance in 10 c.c. of alcohol (or if it is very stable, directly in sulphuric acid) decompose by zinc-dust, add 10 c.c. of acid, and warm until all alcohol is got rid of; when this is accomplished, add 10 c.c. of the acid mixture together with mercury, and then proceed as with an ordinary compound. When distilling with sodium hydroxide, special care must be taken to avoid shaking the flask; it is therefore advisable to apply heat by means of a sand-bath; in the same manner nitroso- and azo-compounds may be readily analysed. Hydrazo-compounds must first be converted into azo-compounds, before exposing them to the action of the sulphuric acid. The author, for example, heats the sulphate of phenylhydrazine first with excess of cane-sugar in presence of sodium acetate for some hours on a water-bath; after drying the resulting mass, the acid may be added. Most cyano-compounds, as far as the author is aware, can be analysed by this process, but some may exist which will not bear the method.

E. W. P.

Notes on Nesslerising. By J. M. Milne (*J. Soc. Chem. Ind.*, **6**, 33).—The author recommends Hehner's method in which the nesslerising is conducted in graduated cylinders having a somewhat broad foot, a glass tap being fused into their sides near the bottom, so that the solution, either standard or water distillate, may be run out until the two tints correspond. This method, a description of which was given in *Chem. News*, **33**, 185, is very simple and readily carried out. As nesslerising cannot be done in gaslight, the author proposes to imitate the process with two shades of indigo solution. D. B.

Estimation of Ammonia in Soils by the Knop-Wolf Method. By A. Baumann (*Landw. Versuchs-Stat.*, **34**, 259—276).—A reply to Knop (*ibid.*, **33**, 438).

Moisture and Free Acid in Superphosphates and similar Fertilisers. By J. Ruffle (*J. Soc. Chem. Ind.*, **6**, 327—333).—It is shown that the soluble phosphoric acid existing in superphosphates is not entirely present as monocalcium phosphate, and that exposure to 100° drives off more than the true moisture, that is, the adhering uncombined water. It is recommended to determine the moisture in the following manner:—Weigh out 2 to 5 grams of the superphosphate in its natural state on a double watch-glass, place under an air-pump over dry calcium chloride, exhaust, then leave for 18 to 24 hours and weigh. The author shows that the acidity of ordinary superphosphates and ammoniated superphosphates is due to phosphoric acid, and not to sulphuric acid. In ammoniated superphosphates, monocalcium phosphate is substantially absent, the free acid being phosphoric acid. D. B.

Detection of Small Amounts of Carbonic Anhydride and other Gases. By O. Rössler (*Ber.*, **20**, 2629—2631).—A small test-tube is drawn out at the lower end to a capillary; this is bent upwards, and cut off at a distance of 1 cm. from the bend. A capillary funnel is then made of such a size that the upper end fits the test-tube, the lower end being at a distance of 1·5 to 2 cm. from the bottom. The substance to be tested for carbonic anhydride is put into the outer tube, the capillary funnel containing baryta-water fitted, and the lower end of the apparatus then dipped into hydrochloric acid. With 0·0005 gram of sodium carbonate a very distinct turbidity, with 0·00005 gram a distinct turbidity is produced in the drop of baryta-water at the end of the capillary. It is possible to detect 0·02 milligram of carbonic anhydride. Sulphuric and nitric acids, hydrogen sulphide, ammonia, &c., can also be detected by means of the apparatus, using iodide of starch, ferrous chloride, lead acetate, and copper sulphate respectively. A sketch of the apparatus is given. N. H. M.

Absorption of Carbonic Oxide by Cuprous Chloride. By H. Drehschmidt (*Ber.*, **20**, 2752—2755).—Hempel has recently shown that in certain cases when cuprous chloride is used as an absorbent of carbonic oxide in gas analysis, there is an increase instead of a decrease of volume. This result is explained on the supposition that the ethylene contained in the absorption-liquid is driven out by the absorbed carbonic oxide. It is here shown that this explanation is not sufficiently valid, as similar results were obtained with mixtures of carbonic oxide, with hydrogen, or nitrogen only. Experiments are described in which a given volume of hydrogen was added to the volume of gas obtained after some of the carbonic oxide had been absorbed; on completing the absorption, a fresh quantity of carbonic oxide was added, and the experiment repeated. In all cases, whether an ammoniacal or hydrochloric acid solution of cuprous chloride was used, an increase of volume of the hydrogen was observed, the increment being greater in the case of the acid solution. It is advisable, therefore, when carbonic oxide is present in small quantities, to use a fresh ammoniacal solution, or to burn with air by means of palladium asbestos. If the amount of carbonic oxide is large, a portion of the gas is unabsorbed, and must subsequently be determined by the above methods. V. H. V.

Estimation of Potassium by Reduction of the Platinochloride with Sodium Formate. By WOUSSEN (*Ann. Agronom.*, **13**, 431—432).—The author has made Corenwinder's process workable by securing the agglutination of the reduced platinum. The modified process is conducted as follows:—So much of the substance should be taken as will yield 0·750 to 1 gram of reduced platinum from the potassium platinochloride. This is precipitated with 18 c.c. of a solution of platinum tetrachloride, containing 200 grams per litre, and a slight excess of nitric acid; 8 to 10 c.c. of hydrochloric acid is added, and the solution evaporated to dryness on the water-bath, then taken up with a mixture of nine-tenths alcohol of 96°, and one-tenth ether, filtered, and washed with the same mixture. The mixture of potassium platinochloride and salts remaining on the filter is treated with a jet of boiling water, and the hot solution of the platinochloride thus formed added in portions to a boiling solution of 2 to 2·5 grams of sodium formate in 10 c.c. of water. The boiling is continued for 15 to 20 minutes, and then 8 c.c. of hydrochloric acid is added, and the boiling continued with constant agitation. After this addition the reduced platinum soon agglutinates, and leaves the solution clear; the metal is collected, washed with boiling water, dried, and weighed.
J. M. H. M.

Estimation of Potash in Commercial Manures. By D. LINDO (*Chem. News*, **56**, 163—165).—Gladding has proposed the following method for this purpose:—Boil 10 grams of the manure for 10 minutes with 300 c.c. of water, when cool precipitate by means of a slight excess of ammonia, make up to 500 c.c., and filter. Evaporate 50 c.c. of the filtrate nearly to dryness, add 1 c.c. of dilute sulphuric acid (1 : 1), continue the evaporation to dryness, and ignite. Dissolve the residue in hot water and a few drops of hydrochloric acid, add 5 c.c. of a 2 per cent. solution of sodium chloride and an excess of platinum chloride solution and wash the precipitate successively with alcohol, solution of ammonium chloride (saturated with potassium platinochloride), and finally again with alcohol, dry, &c. The author has made numerous experiments with this method, and finds it simple, more expeditious, and seemingly susceptible of greater accuracy than the methods usually employed.
D. A. L.

Estimation of Sodium Hydroxide in Soda-ash. By R. WILLIAMS (*J. Soc. Chem. Ind.*, **6**, 346).—The following method is found to give accurate results:—A weighed quantity of soda-ash is agitated with strong alcohol in a stoppered flask and left over night; the undissolved carbonate is filtered off and washed with strong alcohol until a drop gives no alkaline reaction; the filtrate and washings are then titrated with normal acid.
D. B.

Estimation of the Relative Amounts of Sodium Hydroxide and Carbonate in Commercial Soda-ash. By P. HART (*J. Soc. Chem. Ind.*, **6**, 347).—The sample under examination is titrated with standard acid, using phenolphthaleïn as indicator. As soon as the colour disappears, the whole of the hydroxide and one half of the soda existing as carbonate has been neutralised, the number of c.c. being noted. To the same solution (in which the soda now exists as sodium hydrogen carbonate) a little methyl-orange is added, and the addition of acid from the same burette continued to neutral reaction. By doubling the difference between the two titrations and deducting the number from the number of c.c. consumed, the quantity of hydroxide in the original sample is obtained. D. B.

Analysis of Alum Cakes. By R. WILLIAMS (*Chem. News*, **56**, 194—195).—The author has adopted the following methods:—For alumina: neutralise the solution with sodium carbonate, add a large excess of sodium hyposulphite, boil for some time, wash, dry, ignite, and weigh the precipitate. For free sulphuric acid: digest all night with strong alcohol, and titrate the alcoholic extract directly with decinormal soda, using phenolphthaleïn as indicator. Evaporating off the alcohol gives rise to loss, low results are likewise obtained if the digestion is not continued for a sufficient time. In another method, a weighed quantity of quinine, morphine, or strychnine is treated with a known quantity of alum solution, and the alkaloïd reweighed after the treatment, the loss representing the alkaloïd dissolved by the free acid. Comparative results were obtained as follows:—

	Alcohol.	Strychnine.	Quinine.	Morphine.
Free H_2SO_4 per cent...	0·41	0·54	0·50	0·51

The alkaloïd results are all higher than the alcohol, probably on account of some alkaloïd being dissolved by the alum solution and reckoned as sulphate. D. A. L.

Determination of Minute Quantities of Iron, with Special Reference to Alum and Aluminium Sulphate. By R. R. TATLOCK (*J. Soc. Chem. Ind.*, **6**, 276—279).—As a standard, a solution of iron-alum is used, of which 1 c.c. equals 0·001 gram iron. Place 1 gram of the finely powdered sample in an ordinary stoppered sample-tube of about 30 c.c. capacity, and having three marks at 7·5, 10, and 20 c.c. respectively. Add 1 c.c. of standard sulphuric acid, and make up to the lowest mark with water. When the alum under examination is dissolved, add 0·2 gram of ammonium thiocyanate and make up to 10 c.c. with water. Place 1 c.c. of the standard iron solution in a 100-c.c. flask, and make up to the latter volume with water. Now place 1 c.c. of this diluted solution in a stoppered sample-tube, add 1 c.c. of standard acid, make up to the lowest mark with water, add 0·2 gram of the thiocyanate, and make up to the 10 c.c. with water. Then fill up both tubes to the 20 c.c. mark with ether, and agitate them thoroughly. As soon as the contents settle, compare the tints, and if unequal make one or more further trials with greater or less quantities of standard iron solution until the two tints correspond. D. B.

Detection and Estimation of Organic Substances. By J. H. SMITH (*J. Soc. Chem. Ind.*, **6**, 98—111 and 260—271).—When potassium permanganate is used as an oxidising agent in organic research, impure products are obtained, and in varying proportions depending on the amount of reagent employed, temperature, and other conditions. It has therefore only been generally employed as a qualitative reagent. From a study of the behaviour of solutions of various organic substances in presence of a large excess of potassium permanganate under varying standard conditions, it occurred to the author that by employing an excess of the reagent, definite and simple compounds would be obtained whose composition in each case might be determined qualitatively by ordinary analysis, and quantitatively by an estimation of the oxygen absorbed in the reaction. The determinations which the author had in view were the following:—Oxygen yielded by excess of manganese dioxide in acid, alkaline and neutral solutions respectively; oxygen yielded by excess of permanganate in such solutions. The latter would include the former, the difference would represent oxygen yielded by permanganate in reduction to manganese dioxide only, and would necessarily correspond with more stable compounds than those represented by the reduction of manganese dioxide. The author further anticipated successive oxidations, more especially of a neutral one succeeded by an alkaline and acid one respectively, and an alkaline oxidation followed by one in acid solution.

It was found, however, that on oxidising an organic or other oxidisable solution by a large excess of permanganate in acid solution, the results generally came out much too high, even for perfect oxidation, which indicated a loss of oxygen due to the presence of manganese dioxide. In order to prevent or diminish the loss, a ferric salt was added to the permanganate solution, the iron acting as an accelerator in the presence of much permanganate and little manganese dioxide, and a retarder when the conditions were reversed. The ferric salt is really an accelerator, but it has the power of neutralising the action of the manganese dioxide after a certain excess has been formed. The accelerating action of iron in presence of much permanganate may be checked by the addition of sodium phosphate to the solution.

The author has based a quantitative method of estimating organic products on the results obtained from this investigation. The method, which is described in detail in the original, is applicable to the estimation of commercial organic substances, the determination of the organic matter in potable waters and in the waste liquors from works employing organic products, whilst for the estimation of alcoholic solutions when largely diluted, it is more rapid than the sp. gr. method.

In the second part of the paper, the author treats of the oxidation of organic substances by means of manganese dioxide in acid solution, as well as of oxidations by permanganate in neutral and alkaline solutions, and of analytical methods derived therefrom. D. B.

The Stalagmometer: a New Method for the Determination of Fusel Oil in Spirituous Liquors. By J. Traube (*Ber.*, **20**, 2644—2655).—The author previously described (Abstr., 1886, 743) a method for determining fusel oil in brandy by observing the height of the solution in a capillary tube. In the present paper an apparatus, called a "stalagmometer," is described by means of which the percentage of fusel oil is determined by counting the drops contained in a known volume of liquid. As in the older method, the brandy is first diluted so as to be about 20 per cent. It is then put into the stalagmometer, and the number of drops from a given volume observed and compared with the number obtained from the same volume of pure 20 per cent. alcohol. An excess of 1·6 drop to 100 c.c. of liquid shows the presence of 0·1 per cent., an excess of 3·5 drops, of 0·2 per cent. of fusel oil. 0·05 per cent. of fusel oil can be determined readily and with certainty.

To increase the delicacy of the method, the proportion of alcohol to fusel oil must be diminished. This is done in the following manner:—300 c.c. of the liquid to be examined (diluted to 20 to 25 per cent.) is shaken in a funnel with 110 to 120 grams of pure ammonium sulphate, and left until two layers are formed; the lower layer, which contains very little fusel oil, is drawn off and shaken with two to three drops of ethyl alcohol or some crystals of ammonium sulphate. In this way the rest of the fusel oil is obtained as a separate layer. These upper layers are now mixed, dissolved in water, and distilled to about two-thirds. The distillate is made up to 110 c.c., the alcohol determined by means of a Westphal's balance, and the number of drops contained in the volume V by means of the stalagmometer. The latter number is compared with that obtained from pure spirit containing a known amount of fusel oil.

A sketch of the apparatus is given, as well as results obtained by means of it. These show that the method is as accurate as that previously described (*loc. cit.*), the new method having the advantage of being more easily worked. N. H. M.

Assay of Commercial Carbolic Compounds. By J. Muter and L. de Koningh (*Analyst*, **12**, 191—195).—*Carbolic Powders.*—Where the phenols exist in the uncombined state, they are extracted by methylated spirit from 75 grams of the powder. Where the powder contains a lime base, a preliminary thorough trituration with a small excess of dilute sulphuric acid is necessary. The alcoholic extract is mixed with 200 c.c. of a 5 per cent. solution of sodium hydroxide, and the mixture is then evaporated to half its bulk. At this point any tar oils and naphthalene will separate and are to be filtered off. The filtrate is further concentrated to 50 c.c. and transferred to a graduated tube. This, which is known as Muter's carbolimeter, is wide in the lower portion. At 65 c.c. it is narrowed to a neck, which is graduated up to 110 c.c. in 0·25 c.c. divisions. It is stoppered, and is furnished with a long, thin, stirring rod, the volume of which must be allowed for. The solution is made up to 65 c.c., 25 c.c. of strong hydrochloric acid are slowly added with stirring, and then enough dry common salt to render the phenols insoluble. The tube is plunged into water of 15·5° and the volume of the phenols read off.

Liquid Carbolic Acid.—If this contains excess of water, it will not give a clear solution with three volumes of benzene. The amount of water is ascertained by shaking 20 c.c. of the sample with 80 c.c. of a saturated solution of sodium chloride, and observing the diminution in volume. Tar oils are estimated by shaking 20 c.c. with 80 c.c. of soda solution (5 per cent.), and a small quantity of benzene (10 c.c. for dark specimens, less for pale ones). The increase in the volume of the benzene gives the amount of tar oils. The remainder is taken as phenol and cresols. M. J. S.

Acidimetry with Red Wines. By TONY-GARCIN (*Compt. rend.*, **105**, 577).—When red wine, prepared in the ordinary way and not more than a year old is mixed with sodium hydroxide solution, the colour changes to carmine, which becomes deeper and duller and passes into violet-black, which afterwards becomes black, without any tinge of violet, and then changes to green, with formation of a dark, flocculent precipitate. The point at which the colour is brownish-black, without any tinge of violet or green, is the point of exact neutralisation. C. H. B.

Dairy Products. (*Bull. U. S. Agric. Depart.*, No. **13**, 1—128).—*Butter and its Substitutes.*—A series of micro-photographs is given, showing the appearance presented by butter, &c., when examined by polarised light. The black cross described by Hehner and Angell is seen in all the specimens of butter prepared by boiling and slow cooling, and is almost uniformly absent from the crystals obtained from the other fats, nevertheless it is shown by some specimens of butterine and oleomargarine from Armour and Co., Chicago, as well as in a slide prepared from beef suet "oleo oil," by dissolving in hot alcohol, and cooling slowly, thus confirming the opinion that it is not to be trusted as a characteristic of genuine butter.

The following method for determining the melting point of fats is described :—Thin discs are obtained by dropping the melted fat on to a piece of ice. One of these is placed in a test-tube, the lower part of which contains boiled water, and the upper part strong alcohol. The disc floats between the two liquids. The tube is then warmed in a water-bath, whilst the temperature of the contents is taken by a thermometer with small bulb, situated just above and close to the disc, and kept in motion like a revolving pendulum. The temperature at which the disc contracts to a sphere is taken as the melting point. It is necessary to examine the discs when freshly made, as they show a higher melting point if kept for 24 hours. When the water-alcohol tube is warmed before dropping in the disc, the contraction takes place some 6° lower than when the former method is followed.

Various modifications of Reichert's process are described. Davenport saponifies 5 grams of the butter with only 10 c.c. of alcoholic potash (containing 2 grams of KHO), operating in a flask from which the alcohol vapour is aspirated by a water-pump. Saponification and evaporation to dryness are complete in 15 minutes, and from the statement that genuine butters treated thus require on an average 28·8 c.c. of $\frac{N}{10}$ alkali, there would appear to be no loss of ethyl butyrate (compare Allen, Abstr., 1887, 1145). Crampton substitutes phosphoric for sulphuric acid in the distillation, but finds that with care the two give identical results.

Scheffer's test for foreign fats is based on the solvent action of a mixture of amyl alcohol (40 vols.) and ether of sp. gr. 0·715 (60 vols.). 1 gram of butter dissolves in 3 c.c. of this mixture at 28°; 1 gram of lard requires 16 c.c.; 1 gram of stearin 350 c.c.

The following order of value is assigned to the various modes of examining butters for adulteration:—(1.) Determination of volatile acids. (2.) Determination of specific gravity. (3.) Determination of saponification equivalent (Koettstorfer). (4.) Determination of the insoluble acids (Hehner, Muter, Blyth, &c.). (5.) Determination of the melting point.

A complete bibliography of butter analysis (up to 1882) is given by Caldwell (*Second Ann. Rep. N. Y. S. Bd. of Health*, 544—547), and in Sell's Kunstbutter (*Arbeit a. d. Kaiserl. Gesundheitsamte*).

Milk.—For the determination of water, Babcock employs asbestos to absorb the milk before drying; this is much to be preferred to any powder. By placing the asbestos in a tube between plugs of cotton-wool, and drawing air through the tube while it is heated at 100°, the desiccation is complete in two hours. The tube can then be transferred to the fat extractor.

Of methods for the determination of the fat, the preference is given to that of Adams (Abstr., 1886, 583), but instead of soaking up the milk with one end of the roll of paper, the plan has been adopted of holding the unrolled strip in a horizontal position, and running the 5 c.c. of milk from a pipette along the middle. The strip is then hung up in a hot chamber, and in two or three minutes is dry and ready for rolling up.

In Soxhlet's aräometric method (Abstr., 1881, 656) great difficulty was encountered in ensuring the separation of the ethereal fat solution, and any long delay in the separation was found to affect the final results. By placing the bottles containing the mixture in a centrifugal machine revolving about 300 times per minute, the time required for separation was reduced to a few minutes, only six samples out of 150 requiring more than quarter of an hour. The fat solution thus separated had, however, a lower specific gravity than that obtained by simple subsidence, so that the percentage of fat as given in Soxhlet's table had to be increased by 0·13, to bring it into agreement with the results of the older method. Cronander also separates the fat by shaking the milk with potash and ether, but evaporates the ether after it has risen to the surface of the milk, and measures the fat by forcing it in a melted state into a graduated tube.

Fleischman and Morgen calculate the fat by the formula—

$$f = 0{\cdot}833t - 2{\cdot}22\,\frac{100S - 100}{S},$$

where f = percentage of fat, t = percentage of total solids, S = specific gravity of the milk at 15°.

Morse and Piggot add 10 c.c. of milk to 20 grams of dehydrated copper sulphate. The milk becomes dry in a few moments. The fat is then extracted by light petroleum, and its amount determined (after evaporation) by saponification.

Of lactoscopes, Feser's is said to be the most convenient. It is a graduated glass cylinder, containing in its lower part a smaller cylinder of white glass with black lines on it. 4 c.c. of milk are put in the cylinder, and water is added until the black lines become visible. The reading of the total volume gives at once the percentage of fat.

For the determination of the free acid in koumiss, a bright filtrate was obtained by adding to the koumiss an equal volume of alcohol before filtering. M. J. S.

Extraction of Fats by Soxhlet's Apparatus. By J. M. MILNE (*J. Soc. Chem. Ind.*, **6**, 34).—In using the apparatus for milks, the author proceeds as follows:—About 10 c.c. of the milk is weighed into a tared porcelain basin, and the milk evaporated with frequent stirring in order to render it granular, until on being cooled the residue is semi-solid. The residue is then transferred to a paper cup and placed into the Soxhlet tube, and the fat extracted with ether in the usual way. The author having worked with Adams' paper coils for drying up milk for fat extractions, confirms the fact pointed out by the committee of the Society of Public Analysts, that from 0·3 to 0·5 per cent. more fat is extracted by the coil method. D. B.

Examination of Wines and Oils. By P. SPICA (*Gazzetta*, **17**, 304—312).—The author at the outset makes the oft-repeated complaint that the conditions, such as the variation of concentration, or even the nature of the acids used, required for the successful application of test-reactions, are not defined with sufficient exactness in original papers. Various processes have been proposed to recognise the colouring matters, whether natural or artificial, of wines; but preference is given by the author to the methods proposed by Cazeneuve (Abstr., 1886, 397), Arata (*Gazzetta*, **17**, 44), Blarez and Deniges (Abstr., 1886, 1084), and Girard and Gautier. In the last-named process the substitution of tablets of *Magnesia alba* for those of plaster of Paris is suggested; these are immersed in egg albumin for a short time and dried. A drop of the wine to be examined is let fall on such a prepared tablet, and the colour of the stain produced is observed. The natural colouring matters of wine give a yellowish-brown, those containing rosaniline or "vinoline" a reddish-yellow, those with indigo an azure-green, with orchil a violet red, and those with amaranth a greyish-violet stain. Another method suggested consists in shaking up the wine with baryta-water and amyl alcohol, when the latter extracts the colouring matter from the wine. It appears that certain preparations containing coal-tar colouring matters, called "vinoline," are sold by druggists in Padua. An examination of such a preparation, called "maroon vinoline," was found to consist of about 40 per cent. of mineral matter, in which arsenic was present in considerable quantities.

As regards the method of examination of oils proposed by Maumené, which is founded on the rise of temperature when the sample is mixed with concentrated sulphuric acid, it appears that a confusion has arisen between grams and cubic centimetres. Concordant results are obtained with mixtures of 50 grams or 55 c.c. of oil with 10 c.c. of acid.

Bechi has proposed a method for the recognition of cotton-seed oil in olive oil, which consists in adding to the oil an alcoholic-ethereal solution of silver nitrate in presence of an amyl alcohol solution of petroleum; it is here shown that this method gives fallacious results. A method of the greatest practical value is that proposed by Hubl, which has given satisfactory results in the hands of Moore, Allen, Oglialoro, and other observers. V. H. V.

Gravimetric Estimation of Tannins. By H. R. PROCTER (*J. Soc. Chem. Ind.*, **6**, 94—96).—The process described by the author is a combination of the methods published by Müntz and Simand, and depends on the fact that in filtration through a column of dry hide powder the upper layers absorb most of the tannin, a very complete and rapid separation being obtained from the large surface exposed. The author utilises the lamp chimneys employed in the common round-wicked German petroleum lamps, which are contracted just above the base of the flame and are cylindrical for the remainder of their length. A perforated disc of cork is made slightly cup-shaped on its two faces. A piece of linen is then stretched over it, and it is pressed down the chimney until it rests on the contracted neck. Five grams of hide powder is weighed into the tube, and when shaken down will occupy a space of about 50 c.c. The tube is now cut off, allowing only length for the insertion of a cork, which may press slightly on the powder, as it contracts in volume when wet. This cork is perforated and hollowed like the first, and after being covered with linen is pressed into the tube. A short piece of quill tubing passes through the cork, and is fitted by a second cork into a flask. The filtering tube is inverted, broad end downwards, into a beaker of 100 c.c. capacity, which is filled with the liquid to be filtered until it rises into the hide powder. The tube is left in this position for one or two hours, after which it is reversed, and the enlarged end filled with the solution, when the filtration will be found to proceed evenly and steadily. The filtrates thus obtained are perfectly free from tannin, and tested by the Löwenthal method show a lower result for "non-tannin" than those by any other method of absorption. The method is, however, inapplicable in the presence of gallic acid, the latter being freely absorbed by hide powder. The author hopes to overcome the difficulty either by some method of removing the gallic acid or of preventing its absorption by the hide.

D. B.

General and Physical Chemistry.

Relation between the Composition and Absorption-spectra of Organic Dyes. By H. W. Vogel (*Ber. Akad. Ber.*, 1887, 715—718).—Experiments made with azo-dyes gave the following results:—The substitution of methyl for hydrogen in diazobenzene gives rise to change of position of the absorption-bands towards the red end of the spectrum. The increase of wave-length is 10 millionths mm. when the substitution takes place in the ortho-position, and 14 millionths mm. in the case of the para-position. (2.) The substitution of β-naphtholsulphonic acid S or β-naphtholdisulphonic acid R for β-naphtholsulphonic acid B, causes a shifting of the bands which, in the case of β-naphtholsulphonic acid S amounts to 4 to 5 millionths mm., and in the case of β-naphtholdisulphonic acid R to 6 millionths mm. (3.) In the substitution of methyl, the space between the two bands becomes clearer, and the bands become more equal in intensity and in width. The substitution of β-naphtholsulphonic acid S or β-naphtholdisulphonic acid R, in the place of the acid B, acts similarly on the character of the bands.

The above results were obtained with sulphuric acid solutions; the results, as well as those obtained with alcoholic solutions, are shown in tables. N. H. M.

Fluorescences with Well-defined Spectra. By L. de Boisbaudran (*Compt. rend.*, **105**, 784—788).—When gallium oxide is employed as a solid solvent of other oxides, it gives fluorescences which are usually much less brilliant than those obtained with alumina, but the results are of the same order. Calcination of the oxide at a very high temperature converts the bands in the spectrum into lines, the spectral groups being displaced towards the red. The brilliancy of the spectrum increases with the time of action of the electric discharge, a result contrary to that obtained with alumina.

Measurements are given of the spectra of the fluorescences of gallium oxide with oxides of samarium, $Z\alpha$ and $Z\beta$. The fluorescence of $Z\beta$ with gallium oxide is very feeble, the difference between $Z\alpha$ and $Z\beta$ being even more strongly marked than when the oxides are mixed with alumina.

A moderately calcined mixture of alumina with praseodymium oxide yields only a very faint trace of a rosy fluorescence, but if the mixture is very strongly heated, it then yields a beautiful fluorescence, the colour of which depends on the time during which the electric discharge has been passing. At first it is violet, but afterwards becomes rose-coloured. The spectrum is complicated, the principal bands, all of which are nebulous, being situated at 6457, 6237, 6162, 6035, and 5212. C. H. B.

Rotatory Power of Solutions of Ammonium Molybdate and Tartaric Acid. By D. Gernez (*Compt. rend.*, **105**, 803—806).—

The experiments previously made with solutions of tartaric acid and sodium molybdate (Abstr., 1887, 540) were repeated with ammonium molybdate. The rotatory power increases regularly as the quantity of ammonium molybdate increases, and is proportional to the quantity of this salt present up to a quarter of an equivalent. Between one-fourth and one-third of an equivalent, the increase of rotation for the same weight of molybdate changes suddenly, and becomes little more than half its original value. The maximum rotation observed is 57 times that of tartaric acid, and corresponds with a proportion of ammonium molybdate equal to one-third of an equivalent, it remains sensibly constant between 42·66/128 and 56/128 of an equivalent of molybdate. With large quantities, the rotatory power diminishes rapidly, and becomes practically constant when one equivalent of molybdate is present.

As in the case of sodium molybdate, the tartaric acid at first combines with the whole of the ammonium molybdate, forming a compound of the composition $8C_4H_6O_6 + 3(NH_4)_2O,7MoO_3,4H_2O$, which is gradually converted into a second compound, containing 6 mols. of tartaric acid and 1 mol. of the molybdate, and this is finally transformed into a third more stable compound,

$$2C_4H_6O_6 + 3(NH_4)_2O,7MoO_3,4H_2O.$$

In the case of sodium molybdate, the maximum rotation is obtained with one equivalent of the salt, whilst in the case of the ammonium molybdate, the maximum rotation is given by one-third of an equivalent. The ammonium salt, however, contains three equivalents of the alkali in the molecule for each equivalent present in the molecule of the sodium salt, and hence in each case the maximum rotation is given by compounds which contain the alkali and the tartaric acid in equal equivalents. C. H. B.

Influence of Light on the Heat Conductivity of Selenium. By M. Bellati and S. Lussana (*Gazzetta*, **17**, 391—405).—The analogies of heat and electric conductivity induced the authors to study the influence of light on the heat conductivity of selenium, the electric resistance of which, as is well known, is diminished on exposure. The plan of experiment consisted in sprinkling the double iodide of copper and mercury on the disc of selenium, on which a circular figure had been blackened with Indian ink. The selenium was heated by the passage of an electric current, which produced at first a dark spot, owing to the change in colour of the double iodide. This subsequently extended into a fairly regular circular figure, the measurement of the diameter of which afforded a means of determining the heat conductivity of the selenium. This method was found to be more practicable than the usual method of melting wax. In all cases, the diameter of the circle was greater when the selenium was exposed to reflected sunlight from which the greater part of the heat rays had been removed by passage through solutions of alum and of ammoniacal copper sulphate. The relation of heat conductivity without and with exposure to light was found to be in the ratio of 1 : 1·1 as the result of several concordant experiments. The same ratio was observed between the electric conductivities without and with exposure to light under conditions similar to those described above. The authors, however, would not insist on this concordance of results in the two phenomena. V. H. V.

Effect of Light on the Conductivity of Selenium. By S. Kalischer (*Ann. Phys. Chem.* [2], **32**, 108).—Of the selenium cells constructed by the author, three in which copper and copper-brass electrodes are used, are found to differ from the rest in their behaviour on exposure to light, the resistance rapidly increasing after undergoing a momentary decrease, and the cell only returning to its normal condition on remaining for some time in the dark. The conclusion drawn from this is, that the cells in question contain a hitherto unknown modification of selenium, the conductivity of which decreases instead of increasing under the action of light. As the author's other cells which do not exhibit the peculiarity described, differ from the above in having zinc, copper-zinc, and copper-platinum electrodes, it still remains to be ascertained whether the nature of the electrodes has any influence on this behaviour of selenium. The phenomenon in question has also been observed and described by Hesehus (*Exn. Rep. d. Phys.*, **20**, 490). H. C.

New Galvanic Battery. By F. Friedrichs (*Ann. Phys. Chem.* [2], **32**, 191).—A tube running below the cells of this battery connects each with a common reservoir, by the raising or lowering of which the fluid used can be transmitted to or removed from the cells. A tap attached at the end of the tube opposite the reservoir allows the fluid to be removed when exhausted. An advantage claimed over other batteries is, that spontaneous evaporation of the liquid and consequent crystallisation of salts when the battery is not in use, is avoided. H. C.

Galvanic Polarisation. By F. Streintz (*Ann. Phys. Chem.* [2], **32**, 116).—The author has examined the galvanic polarisation produced on aluminium and silver plates. The results for aluminium have been already given (Abstr., 1887, 415). With silver, the oxygen plate is found to attain maximum polarisation when the E.M.F. of the cell used is equal to that of three Daniells; the polarisation of the hydrogen plates is at a maximum when an E.M.F. of two Daniells is used, it decreases when a greater E.M.F. is employed, but rises again and becomes equal to the first maximum for an E.M.F. of nine Daniells. The explanation given is that the deposition of metallic silver on the cathode, which is greater the greater the intensity of the current, by increasing the surface decreases the relative strength of the current and amount of the polarisation, so that although a small E.M.F. produces maximum polarisation with clean plates, a very considerable one is required to attain the same maximum with plates thickly coated with silver. H. C.

Production of Electricity by the Condensation of Aqueous Vapour. By L. Palmieri (*Nuovo Cimento* [3], **22**, 34—39).—The occasion of this paper is the confirmation by Firmin Larroque (*La*

Lumière Élect., 1887) of the author's experiments on the production of electricity by the condensation of aqueous vapour. On the other hand, the experiments of Kalischer (Abstr., 1884, 138) led to negative results, but Tait considers that these were conducted on far too small a scale. Accordingly the author has repeated on a large scale his experiments on the condensation of aqueous vapour on a beaker of platinum containing ice, and connected with a condensing electric cup; in all cases, the production of electricity was observed. The author remarks that his observations, extending over 37 years, leave no doubt in his mind as to the production of electricity under these conditions. The potential of atmospheric electricity is conditioned by the state of the weather; the author's observations also have more particularly shown that the potential is affected by the eruptions at Vesuvius. V. H. V.

Electrolysis of Water. By H. v. HELMHOLTZ (*Ber. Akad. Ber.*, 1887, 749—757).—Previous experiments made by the author showed that the smaller the amount of dissolved hydrogen and oxygen near the electrodes, the smaller the electromotive force necessary to electrolyse water. The experiments described in the present paper were made with a view to determine the limits for the smallest electromotive force capable of producing fresh gas under a given pressure of the oxyhydrogen mixture on the liquid. In previous experiments, an error in the measurement of the electromotive force of the decomposition of water was caused by hydrogen or other combustible gas being occluded in the platinum anode or in both electrodes, so that the oxygen carried over in the current comes in contact with the gases of the anodes, and thus bubbles of hydrogen will be liberated at the cathodes with a much less expenditure of electromotive force. To avoid this, the current is kept in the same direction for weeks or months. An apparatus is described with sketch, by means of which the gases produced by the electrolysis are removed as soon as formed, and a vacuum is thus kept above the liquid; the flask containing the solution is so inclined that a small bubble of gas is retained; the gas under these conditions occupies a space 1000 times greater than it would under normal pressure, and the diameter of the bubble is measured in order to ascertain whether it remains the same size or whether it increases.

To produce a current, three carbon-iron ferric chloride solution elements were used; the electromotive force was diminished daily in order to determine the limit. The limit for the evolution of gas was found to be 1·64 to 1·63 volt, with a pressure of oxyhydrogen gas = 10 mm. of water.

The influence of pressure on electromotive force is expressed as follows:—

$$A = A_o + 10^{-7}.\eta.\theta\left\{R_h \frac{2\alpha_h}{2\alpha_h + \alpha_o} \log\left(\frac{p_h}{p_a}\right) + R_o . \frac{\alpha_o}{2\alpha_h + \alpha_o} \log\left(\frac{p_o}{p_a}\right)\right\}.$$

p_a = atmospheric pressure, p_h and p_o are the pressures of hydrogen and of oxygen above the liquid; a_h and a_o are the atomic weights of the two elements; θ is the absolute temperature.

$$R_h = \frac{p_h \cdot v_h}{\theta} = 41461000 \cdot \frac{cm^2 . q}{sc^2},$$

where v_h is the volume of 1 gram of hydrogen; R_o the corresponding constant for oxygen, and η the amount of water decomposed in a second by one Ampère. $\eta = 0{\cdot}00009319$ according to Kohlrausch.

When pure oxyhydrogen gas is above the liquid, as in the experiments described, $p = p_h + p_o$, the part of the electromotive force changing with the pressure becomes—

$$A_1 - A_2 = \frac{1}{6} . 10^{-7} . \eta . \theta . R_h . \log \left(\frac{p_1}{p_2}\right) = 0{\cdot}018868 . \log \text{nat.} \left(\frac{p_1}{p_2}\right).$$

N. H. M.

Electrolytic Separation of the Metal on the Free Surface of the Solution of its Salt. By J. GUBKIN (*Ann. Phys. Chem.* [2], **32**, 114).—When an electric current passes from a solution of a salt into the atmosphere of gas or vapour immediately above it, an electrolytic separation of the metal takes place at the surface of the liquid. Apparatus is described by means of which this is made evident, the space above the liquid being either vacuous or exposed to the air in the ordinary way. Silver and platinum are found to separate out in films which float on the surface; zinc oxidises as it separates out, the white flakes of zinc oxide gradually falling to the bottom.

H. C.

Action of the Solvent on Electrolytic Conduction. By T. C. FITZPATRICK (*Phil. Mag.* [5], **24**, 377—391).—The author continues his researches on the conductivity of salt solutions, the solvents being varied. The salts examined were calcium, lithium, and magnesium chlorides and nitrates, and ferric and mercuric chlorides, the solvents being water and ethyl and methyl alcohols. Tables of conductivities are given. With mercuric chloride, which is the only salt more soluble in alcohol than in water, the conductivities are little more than those of the solvents alone. For aqueous solutions, the chlorides conduct better than the nitrates; magnesium chloride is anomalous, its conductivity being half that of calcium chloride. Ferric chloride in dilute solution shows signs of dissociation. With alcoholic solutions, the conductivity is not proportional to the amount in solution. The conductivity of lithium salts in ethyl alcohol is 10 to 20 times as great as that of the other salts. In all cases, the aqueous solutions conduct better than the alcoholic ones, the character of the solvent appearing to have an influence on the conductivity. This the author considers to be due to the formation of molecular groups in the solutions. He finds that the conductivity of salt solutions at low temperatures points to the existence in solution of cryohydrates at temperatures above their solidifying points, and also that the conductivity of mixed solvents and of salts in mixed solvents differs from the calculated values, showing that an interaction has taken place with formation of new molecular groups. The action then of the solvent is twofold: (1) decomposition of the salt, the amount depending on the temperature, nature of solvent, and state of dilution; (2) the formation of fresh molecular groups in the solution.

H. K. T.

Influence of a Magnetic Field on the Thermoelectric Properties of Bismuth. By G. P. Grimaldi (*Nuovo Cimento* [3], 21, 57).—It is well known that a magnetic field influences in a remarkable degree the electric resistance of bismuth; in this paper, the author shows that its thermoelectric force when paired with copper is varied in a similar degree. This pile was placed in the field of an electromagnet, and coupled up with a galvanometer, in which readings were taken without and with a current passing round the electromagnet. After due allowance for induction, it is shown that the thermoelectric force of the bismuth-copper pair is materially decreased in the magnetic field. The experimental enquiry is, however, only in the preliminary stage. V. H. V.

Rotation of Isothermic Lines of Bismuth placed in a Magnetic Field. By A. Righi (*Gazzetta*, 17, 359).—In the course of experiments on the heat conductivity of bismuth when placed in a magnetic field, it was observed that the isothermic lines were rotated in a direction opposite to that of the magnetising current when a rectangular strip of the metal was placed with its planes normal to the line of force. The phenomenon is analogous to that observed by Hall, namely, the rotation of the equipotential lines when a magnet acts on a current flowing along a thin strip of metal, and may explain the thermomagnetic currents recently discovered by Ettingshausen.

V. H. V.

Thermic Conductivity of Bismuth in a Magnetic Field. By A. Righi (*Gazzetta*, 17, 358—359).—The author, as well as other physicists, has observed the marked variation of the electric conductivity of bismuth when placed in a magnetic field (Abstr., 1887, 1009), and the production of Hall's phenomenon under these conditions. Considering the correlation of electric and thermic conductivity, the effect of magnetic field was also studied; the results of the experiments showed that with a field of 4570 C.G.S. units the thermic conductivity of bismuth is to that of the metal under ordinary conditions as 1 : 0·886. This result must at present be only considered as approximate; further experiments are being made with more refined apparatus. V. H. V.

Specific Heat of Superfused Water. By P. Cardani and F. Tomasini (*Nuovo Cimento* [3], 21, 185).—The specific heat of water at various temperatures has been the subject of numerous investigations, although the results obtained are far from concordant. Thus at temperatures 0—10°, Hirn, as also Pfaundler and Platter, has observed a marked increase of specific heat, whilst Rowland on the other hand observed a decrease. In this paper, a description is given of experiments made to determine the specific heat of water in the superfused condition. The method adopted in the investigation is practically an application of the weight thermometer; a known volume of water is enclosed by mercury within a bulb, connected with which is a capillary tube bent twice at right angles. The whole apparatus is completely filled with water and mercury, and the bulb cooled by suitable freezing mixtures, then the mercury driven out by the expanding water is collected and weighed. The apparatus is then agitated, and the mercury driven out by the solidification of the water is also collected and weighed. Then from these data, together with a determination of the temperature at the moment of solidification, and the quantity of heat absorbed by the glass and the mercury contained, the specific heat of the water at the temperature of solidification is ascertained. The various experimental errors are discussed in full, and the data of all the observations given in a series of tables. The following are the main conclusions: the specific heat of superfused water is less than unity; it increases with decrease of temperature from a minimum at a temperature of −6·52° to 0°. The final results are given below.

Temperature.	Specific heat.
−6·52° to 0°	0·953
−8·09 „ 0	0·961
−9·47 „ 0	0·962
−10·67 „ 0	0·985

V. H. V.

New Form of Calorimeter. By W. F. Barrett (*Proc. R. Dublin Soc.*, 5, 13—16).—The instrument devised by the author is a modification of Bunsen's calorimeter. The cup for holding the substance under experiment forms part of a mercurial thermometer. The cup has a capacity of 4 c.c., and is surrounded by a jacket of polished metal. The stem of the thermometer, of which the cup is a portion, is supported horizontally, and graduated from −5° to 80°. Supported immediately above the cup is a small burette, the level of the liquid in which can be accurately read. The neck of the burette may be closed by a short thermometer graduated from 30° to 100°. In making a determination of the specific heat of a liquid with this instrument, the weight of the liquid must be found by taking its specific gravity for the temperature at which it was used; the volume of the liquid used having been read from the burette. This inconvenience may be obviated by converting the thermometer into a balance, the stem being supported by knife-edges somewhere near its centre of gravity. From the end of the stem, a pan is suspended, and beyond this a pointer, fixed to the stem, moves over a graduated arc. With a calorimeter balanced in this way, the weight of the liquid at a given air-temperature may be found directly. B. H. B.

Determining the Specific Gravity of Small Quantities of Dense or Porous Substances. By J. Joly (*Proc. R. Dublin Soc.*, 5, 41—47).—The method generally employed for determining the specific gravity of small quantities of minerals of low density is by balancing in a liquid of known specific gravity. This method, however, is inapplicable when the substance has a specific gravity over 4, and also when the substance is of a porous nature. Under these conditions, the substance may be mixed with another substance of much lower specific gravity in such proportion that the specific gravity of the mixed substances may be as close to that of either of them as may be desired. For this purpose, the author uses the paraffin sold in the form of candles. The transparency of the paraffin enables the appearance of the embedded mineral to be minutely examined. Results are given showing the accuracy of the method. B. H. B.

Dissociation of Copper Sulphate. By W. MÜLLER-ERZBACH (*Ann. Phys. Chem.* [2], **32**, 313).—The author has studied the dissociation of copper sulphate at higher temperatures than those which he previously employed, and finds that his results agree with those obtained by Lescœur (Abstr., 1887, 208). The paper also contains a discussion of the dependence of chemical affinity on temperature (Abstr., 1887, 628). With sodium phosphate containing 5 mols. H_2O, and sulphuric acid of 1·294 sp. gr., water passes from the acid to the salt at 32°, but the change is reversed, and water passes from the salt to the acid at 47°. The equilibrium between the affinity of copper sulphate and of dilute sulphuric acid for water occurs, as might be expected, at higher temperatures the more dilute the acid.

H. C.

Rate of Dissociation as a Measure of the Vapour-tension of Hydrated Salts. By R. SCHULZE (*Ann. Phys. Chem.* [2], **32**, 329).—A reply to Müller-Erzbach. The author seeks to justify his former conclusions with regard to Müller-Erzbach's method of determining the vapour-tension of hydrated salts (Abstr., 1887, 766). Müller-Erzbach having objected to the use of zinc sulphate as being a salt which admittedly exhibits irregularities in its behaviour, copper sulphate is here shown to act in an irregular manner also when investigated by the above method. In two out of three tubes containing copper sulphate, evaporation set in at 20°, but the third did not exhibit any change even at the end of 10 weeks. H. C.

Interaction of Metals and Sulphuric Acid. By V. H. VELEY (*Chem. News*, **56**, 221—222).—In this communication, the author points out that the results obtained by Spring and Aubin in their investigation on the action of acids on zinc containing lead (Abstr., 1887, 1074) do not adequately represent the rate of chemical change as comparable, for example, with the rate of evolution of a gas from a homogeneous liquid. Thus the initial retardation or "induction" observed may be due to the adherence of bubbles of gas to the surface of the metal, and, secondly, when the change has set in, the metal is surrounded by a concentrated solution of the metallic salt, which is only in part removed by the gas bubbles. The hydrogen evolved is a resultant of a series of changes, each one of which is variable at any moment, such as the rate of diffusion of the salt of the metal in the acid liquid, the amount of surface exposed (which Spring and Aubin in some experiments kept approximately constant), and the local rise of temperature. The amount of gases other than hydrogen, such as sulphurous anhydride and hydrogen sulphide, is doubtless also dependent on the more or less perfect removal of the products of the change from the sphere of the dissolving metal as well as on the concentration of the acid solution. On the other hand, it does not seem that variations in the relative masses of zinc could make any difference either in the rate of solution or in the products of the change, provided that the surfaces exposed were equal. The dissolution of a solid in a liquid must be regarded as a superficial action only. The author is at present studying the rate of solution of metals in acid liquids under such conditions that not only fresh surfaces of a regular geometrical figure are continuously being exposed, but also the products of the change, whether gas or metallic salt, are at once and continuously removed from the vicinity of the dissolving metal.

V. H. V.

Velocity of the Formation of Ethereal Salts. By N. MENSCHUTKIN (*Compt. rend.*, **105**, 1016—1019).—The particular reaction investigated was the action of acetic anhydride on alcohols, $Ac_2O + RHO = AcOR + AcOH$, at 100°. With most alcohols, the reaction is complete. The formation of the ethereal salt is accompanied by a change of volume, which is least with methyl alcohol and increasingly greater with ethyl, propyl, and isobutyl alcohols. In order to eliminate this variable, the mixture of acetic anhydride and alcohol was diluted with 15 volumes of benzene. The constants of velocity are calculated from the equation $\frac{dx}{dt} = C(A - x)(B - x)$, in which A and B are the quantities of the substances originally present, and x the quantity of the new substance formed in time t. A and B being equal, and x and t being 0, $\frac{x}{A - x} = CAt$, which gives the constant C. The results given in the following tables are the mean of several concordant experiments, the constants of velocity being referred to that observed with methyl alcohol, which is taken as 100:—

Primary alcohols.	Constants of velocity.	
Methyl alcohol	0·1053	100·0
Ethyl "	0·0505	47·9
Propyl "	0·0480	45·6
Butyl "	0·0465	44·1
Isobutyl "	0·0401	38·1
Heptyl " (normal)	0·0393	37·3
Octyl " "	0·0377	35·8
Tetradecyl alcohol (normal).	0·0291	27·6
Hexadecyl " "	0·0269	25·5
Octodecyl " "	0·0245	23·2
Melissyl " "	0·0174	16·5
Allyl " "	0·0287	27·2
α-Methyl allyl alcohol	0·0267	25·3
Benzyl alcohol	0·0280	26·6

Secondary alcohols.	Constants of velocity.	
Isopropyl alcohol	0·0148	14·1
Methyl ethyl carbinol	0·0123	11·6
Methyl hexyl „	0·00916	8·7
Methyl allyl „	0·00643	6·1
Tertiary alcohol.		
Trimethyl carbinol	0·00091	0·8

The ethereal salts of the tertiary alcohols, phenols, and propargyl alcohol are decomposed by acetic acid, and hence in these cases the reactions are not comparable with those of primary alcohols.

The greatest velocity is observed with methyl alcohol. The velocity is affected by the isomerism of the radicles in the alcohols, but is highest with primary alcohols, and much lower with secondary alcohols, whilst in the case of tertiary alcohols it is very small indeed. In homologous alcohols of analogous constitution, the constant of velocity diminishes as the molecular weight increases, the difference being greatest in the normal primary alcohols. Non-saturated alcohols have a lower constant of velocity than the corresponding saturated alcohols.
C. H. B.

Inorganic Chemistry.

Action of Carbon Bisulphide on Metals. By A. Cavazzi (*Chem. Centr.*, 1887, 888, from *Mem. R. Acc. Sc. Inst. Bologna* [4], **7**, 27–33).—Carbon bisulphide vapour when passed over the heavy metals in a fine state of division and heated to a high temperature yields metallic sulphides with separation of carbon in a graphitoïdal form. Other compounds of carbon with sulphur seem not to be formed in any case.
V. H. V.

Formation of Hydrates of Lithium Hydroxide from Alcoholic Solutions: Quantitative Determination of Lithium. By C. Göttig (*Ber.*, **20**, 2912—2915).—Lithium hydroxide generally separates from hot saturated solutions in 96·8 per cent. alcohol with ½ mol. H_2O; when in contact with water, it shows the movements previously observed with crystals of potassium and sodium hydroxide (Abstr., 1887, 636).

When lithium hydroxide is crystallised from 62·8 per cent. alcohol, a hydrate with 1 mol. H_2O is obtained; the crystals do not move when placed in contact with water.

In determining lithium as sulphate, the sulphate must be ignited for a long time until of constant weight.
N. H. M.

Transformation of Ammonium Nitrate. By M. Bellati and R. Romanese (*Nuovo Cimento* [3], **21**, 5—24).—Frankenheim, and, more recently, Lehmann have shown that ammonium nitrate crystallises in various forms, according to the temperature at which the crystallisation is effected. Thus at 36° it crystallises in the trimetric system, at 87° in the rhombohedral, and at 120° in the monometric system. In the present paper, it is shown that at these various points the salt undergoes other physical modifications. Thus, on warming, the temperature of the salt increases in direct proportion to the time up to a temperature of 35·67°; so also the rate of cooling is regular up to 30·3°, reaching a minimum at 30·07°; it then increases to 31·05°, at which point it remains constant for some time. Similar phenomena are also observable at a temperature of 85·5° to 86·5° with ascending temperature, and 82·2° to 82·6° with descending temperature, as also at 124·8° and 124·05°.

The variations of volume corresponding with these crystalline changes is also determined in an accurately calibrated dilatometer containing oil of turpentine, a liquid whose expansion is regular, and which, when properly dried, does not dissolve the salt. Results show that the curve of coefficient of expansion has two points of inflection: one at a temperature between 33·29° and 41·29°, and another at about 85°; the formula expressing the rate of expansion from 0° to the former of these points is $v_1 = v_0 (1 + 0·000339t + 0·000000346t^2)$, whilst between 40° and 85° this becomes $v_1 = v_0 (1·04957 + 0·00038756t + 0·000008976t^2 + 0·0000000432t^3)$. There is also an alteration in the value of the mean specific heat at the temperature of these crystalline transformations; applying the method of mixtures and using oil of turpentine as the liquid, it is shown that the mean specific heat from 0—31° is 0·407, from 31° to 82·5° is 0·355, and from 82·5° to 124° is 0·426. Hence the following values are deduced for the heats of transformation at these points:—

At 31·0° = 5·02
„ 82·5 = 5·33
„ 124·0 = 11·86

The values obtained for the specific heats of ammonium nitrate are compared with those of Kopp and Tillinger, and the methods of correction applied by the latter are criticised. V. H. V.

Ammonium Phosphites. By L. Amat (*Compt. rend.*, **105**, 809—811).—A solution of phosphorous acid mixed with ammonia until neutral to methyl-orange, and then concentrated until the weight of the liquid is one-fourth or one-fifth more than the calculated weight of the salt, yields large, deliquescent crystals which can be dried over sulphuric acid or at 100°. Similar crystals are obtained if the liquid is concentrated in a vacuum at the ordinary temperature. The crystals have the composition $NH_4·H_2PO_3$, and seem to be monoclinic prisms; they melt at 123° and are very soluble in water. At 145° they lose half their ammonia without evolution of hydrogen phosphide, and yield a gummy mass which seems to contain crystals. At a higher temperature, ammonia and hydrogen phosphide are given off and phosphoric acid is formed.

Hydrated diammonium phosphite, $(NH_4)_2HPO_3 + 2H_2O$, when kept in a dry vacuum at the ordinary temperature or heated at 100°, loses water and ammonia, and yields the monammonium salt just described. Both at the ordinary temperature and at 100°, the water is given off before the ammonia.

Monammonium phosphite has no appreciable action on ammonia gas at the ordinary temperature, but at 80° to 100° absorption is rapid, and the anhydrous diammonium salt is obtained as a white powder. The corresponding compounds of sodium and potassium have not yet been obtained. C. H. B.

Effects produced by Small Quantities of Bismuth on the Ductility of Silver. By J. Scully (*Chem. News*, **56**, 224—226; 232—244; 247—248).—It is observed that the Indian method of wet assay is incidentally a delicate test for bismuth in presence of a large excess of silver. The bullion is dissolved in nitric acid, the solution diluted, excess of hydrochloric acid added, and the whole vigorously agitated to facilitate the aggregation of the silver chloride, which settles down and generally leaves a clear supernatant liquid; if, however, the liquid is turbid and the silver chloride on exposure to light, while still under the liquid, remains white, the turbidity is due to mercury, if on the other hand, the silver chloride becomes discoloured, the turbidity is due to bismuth; tin and antimony having been proved to be absent when dissolving in nitric acid. In such cases, to prevent the vitiation of the silver assay, the following modified method has proved successful:—The assay pound of bullion is dissolved in 5·5 c.c. of nitric acid, sp. gr. 1·200, the solution is mixed with 5 ozs. of water and 10 c.c. of nitric acid, sp. gr. 1·320, then 2·5 c.c. of hydrochloric acid are added, and the method proceeds as usual. For the estimation of the bismuth, having obtained a rough idea of the amount of bismuth present from the amount of turbidity in the trial assay, sufficient bullion to yield a weighable amount of bismuth is dissolved in a small quantity of nitric acid, the solution diluted and heated with excess of ammonium carbonate, which dissolves the silver and copper carbonates, but leaves the bismuth carbonate insoluble; the latter is then washed, dried, ignited, and weighed. If lead or cadmium are present they would remain with the bismuth carbonate; the latter, however, is not likely to be present, and the former may be separated by dissolving the bismuth carbonate in nitric acid, and evaporating down with sulphuric acid; the lead sulphate is treated in the usual manner and weighed, whilst the bismuth is reconverted into carbonate and estimated as described above.

Fine silver, or silver containing 10 per 1000 of copper, alloyed with 1 to 5 per 1000 of bismuth and cooled rapidly, had its ductility, as tested by rolling, sensibly but slightly impaired, the straps having jagged edges; with 6 per 1000 of bismuth, the decrease in ductility was more evident, whilst fine silver with 9 to 11 per 1000 of bismuth was so brittle as to break with a mere tap. When, however, the cooling was gradual, 4 per 1000 of bismuth was sufficient to make the silver or silver-copper alloy mentioned above highly brittle, the fracture being crystalline in the case of fine silver and granular in the silver-copper alloy. With Indian standard silver containing 83·4 per 1000 of copper, 2 per 1000 of bismuth produced red shortness and jagged straps: as the quantity of bismuth increased the evidence of diminished ductility is more decisive, and with 10 per 1000 of bismuth the alloy was very brittle and had a granular fracture; the mode of cooling had no appreciable effect on the ductility of these alloys. Other experiments with Indian coinage bars show that the ductility of bullion is not materially affected by the presence of 0·5 per 1000 of bismuth.

As the refining fine silver containing bismuth is both tedious and attended with loss of silver, the author suggests dilution with silver free from bismuth as a practical means of overcoming the brittleness. The author remarks on the concordance of his results with those of Gowland and Koga (Trans., 1887, 410—416), as regards the question of brittleness. The discrepancy in reference to refining bismuth silver he suggests is possibly due to the Japanese silver containing more base metals than the Indian silver; it consequently supplied more slagging material and greater facilities for refining.

D. A. L.

Combination of Silver Chloride with Metallic Chlorides.

By M. C. Lea (*Amer. J. Sci.*, **34**, 384—387).—If hydrochloric acid is mixed first with ferric chloride and then with silver nitrate, the silver chloride which forms is not white but buff-coloured. The ferric chloride cannot be removed by washing, and is only partially removed by treatment with hydrochloric acid. The presence of the minute quantity of ferric chloride makes the silver chloride remarkably less sensitive to light.

Cobalt chloride and hydrochloric acid give a silver chloride which is pink and contains cobalt; but the reduction in the sensitiveness to light is very much less than when iron is present. Nickel and manganese behave similarly, but cupric chloride seems to have no tendency to combine with silver chloride. The tendency of gold chloride to combine with the silver chloride is, however, well marked, and the precipitate has a reddish shade, but the influence on the sensitiveness is not easily determined, since the gold is rapidly reduced to the metallic state, and the silver chloride darkens to black instead of to chocolate or violet as would be the case if it were pure.

In analytical determinations, it is important to digest the silver chloride for a considerable time with hydrochloric acid, and even then it is doubtful if the foreign chloride is entirely removed, especially if it is ferric chloride.

These observations show that silver chloride has a great tendency to combine with small quantities of other chlorides, and supports the author's view as to the nature of the "photo-salts" (this vol., p. 1). They also explain the fact that a small quantity of mercuric chloride very greatly reduces the sensitiveness of silver chloride to light. In order to ascertain the presence of mercury in the silver chloride, the author employs a solution of stannous chloride in hydrochloric acid which has no action on silver chloride if light is carefully excluded, but gives a brown or brownish-black colour to the precipitate if mercury is present. The author was unable to remove mercuric chloride from silver chloride even by very prolonged washing.

Poitevin's observation that his coloured photographic images resisted the action of light better after they were treated with dextrin and lead chloride is explained by the tendency of the lead salt to prevent alteration of silver chloride. C. H. B.

Silver Potassium Carbonate. By A. DE SCHULTEN (*Compt. rend.*, **105**, 811—813).—When silver carbonate is formed by the action of an alkaline carbonate on silver nitrate, the precipitate is sometimes white, sometimes yellow, but always becomes yellow when washed. If silver nitrate is added to an excess of a concentrated solution of potassium carbonate containing some hydrogen carbonate, a white precipitate is formed which changes to microscopic crystals of the composition $AgKCO_3$. This compound is decomposed by water, with removal of the potassium carbonate and formation of yellow silver carbonate.

150 grams of potassium carbonate is dissolved in 150 c.c. of water, cooled and agitated with 15 grams of potassium hydrogen carbonate. When the liquid is saturated with the latter salt at the ordinary temperature, it is filtered and mixed with a solution of 1 gram of silver nitrate in 25 c.c. of water. In order to obtain large crystals, the liquid containing the precipitate is heated with continual agitation. The precipitate dissolves, and when the liquid is cooled it deposits long, transparent crystals with a brilliant lustre; sp. gr. 3·769. They do not blacken when exposed to light except in the presence of organic matter, and when treated with water, the silver carbonate which remains retains the form of the original crystals. When heated, the compound loses carbonic anhydride, and at a higher temperature the silver oxide which is formed gives off oxygen.

The crystals are microscopic, rectangular lamellæ with a terminal angle closely approaching 90°. The refraction is almost identical with that of apatite; the extinction of parallel polarised light takes place longitudinally; twinning plane parallel with the plane of the optical axes; sign of elongation positive; maximum birefractive power approximately 0·0216. C. H. B.

Lead Aluminium Sulphate. By G. H. BAILEY (*J. Soc. Chem. Ind.*, **6**, 415).—The author has examined some crystals which have been noticed in a mordanting liquor (aluminium nitroacetate) prepared by dissolving up alum, lead acetate, and lead nitrate in water and allowing to settle. The crystals form octahedra crystallising in cruciform aggregates like alum. They are, however, not transparent and are quite unaltered by exposure to air. The substance is a lead alum, $Pb_2Al_2(SO_4)_5 + 20H_2O$, formed under special conditions of concentration and temperature. D. B.

New Oxide of Thallium. By A. PICCINI (*Gazzetta*, **17**, 450—452).—Carstanjen has observed that when a rapid current of chlorine is passed through a concentrated solution of potash in which thallium sesquioxide is suspended, the solution acquires a violet colour which is considered to be due to a potassium thallate. The same liquid is also formed when thallium hydroxide is submitted to electrolysis, using a plate of thallium as an electrode, as also on adding potassium hypochlorite to a quarter of its weight of caustic potash to which thallium sulphate is subsequently added. On digesting the whole and adding barium nitrate, a violet precipitate is finally obtained. The results of analyses made to determine the relation between thallium and barium in this precipitate led to discordant results, but sufficient evidence was afforded to point to a formula, TlO_2, for the oxide of thallium. The isolation of this oxide brings out a further point of analogy of the thallium compounds to those of lead. Experiments made to prepare the corresponding sulphur compound have not as yet been successful, although substances have been obtained which contain a proportion of sulphur greater than that required for the trisulphide.

V. H. V.

Constitution of Basic Salts. By S. U. Pickering (*Chem. News*, **56**, 210—212).—In the author's opinion, those basic compounds, which although seemingly of indefinite composition can scarcely be regarded as mere mixtures, are precisely analogous to the complex hydrates, which he contends constitute a solution of a salt in water. Hydrated basic salts of copper may be obtained of a composition corresponding with that of an anhydrous salt of the formula $17CuO,SO_3$, but the most basic definite sulphate known is $4CuO,SO_3$, therefore if these higher basic salts are to be regarded as mixtures, they must be mixtures of a basic salt with copper hydroxide and not mixtures of two different basic salts.

To investigate this point, a series of basic copper salts were prepared by diluting a solution of ammonio-copper sulphate with increasing quantities of water; the precipitates were dried in a vacuum, and analysed. The results, although not decisive, tend to show that free copper hydroxide is not present in these compounds, for on comparing any two preparations of different basicity, the excess of copper oxide present in the more basic one is not accompanied by a constant proportion of water.

D. A. L.

Crystallised Mercurous Iodide and Bromide. By A. Stroman (*Ber.*, **20**, 2818—2823).—If a saturated solution of mercurous nitrate, as free as possible from oxide and slightly acidified with nitric acid, is heated to boiling with iodine, the latter becomes covered with a yellow powder, which partially dissolves, and the solution, after decantation into a warm dish, deposits, in the dark, lustrous, yellow, transparent, tetragonal scales of mercurous iodide; these must be dried in the dark at the ordinary temperature. When the mercurous nitrate solution is treated with an alcoholic solution of iodine in the cold, small, yellow spangles of mercurous iodide are obtained, but the product formed by the old methods of preparation, that is, by rubbing together molecular proportions of mercury and iodine, and by adding potassium iodide in solution to a solution of a mercurous salt, have a green colour, and are impure, although the pure yellow compound can be obtained by reversing the last process and adding an excess of a dilute solution of mercurous nitrate to potassium iodide in solution. The crystallised compound shows the same colour-change as observed by Yvon (this Journal, 1873, 1105), but the change does not begin at 60°, as stated by him, since the salt is still a pure yellow at 100°, and only passes from this colour through dark yellow and orange to garnet-red at higher temperatures. Sublimation commences at 110—120°, not at 190° as stated by Yvon, and the salt fuses at 290° with decomposition. Towards acids and solvents, the crystallised compound behaves like that precipitated by potassium iodide; ammonia and caustic alkalis render it green, and on heating convert it into the corresponding alkaline iodide and metallic mercury. The crystallised iodide is less sensitive to light than the precipitated yellow compound, which rapidly becomes black even in diffused daylight.

When mercurous nitrate solution is treated with bromine under similar conditions, small, white, nacreous, tetragonal scales of mercurous bromide are obtained, and the same compound separates in yellow, crystalline spangles when an alcoholic or aqueous solution of bromine is employed. It sublimes at 340—350° in small scales, is less sensitive to light than the iodide, dissolves in hot sulphuric acid with the evolution of sulphurous anhydride, becomes black and gradually decomposes when heated with dilute and concentrated hydrochloric acid, dissolves slowly in hot nitric acid (sp. gr. = 1·42), and decomposes with the formation of the corresponding bromides when treated with ammonia and caustic alkalis.

W. P. W.

Atomic Weight of Yttrium Metals in their Natural Compounds: Gadolinite. By C. RAMMELSBERG (*Ber. Akad. Ber.*, 1887, 549—556).—According to Nordenskiöld (Abstr., 1887, 109), the oxides of the yttrium metals occur in their natural compounds in proportions so nearly constant that he suggests the term gadolinium oxide for this mixture of yttrium, erbium, and ytterbium oxides.

The author shows from the results of 29 analyses of minerals from different sources and by various chemists, that this mixed oxide, so far from being constant, would give atomic weights varying from 97·5—132·5° for the mixture of metals.

Analyses of gadolinite from Hitterö and Ytterby gave the following results:—

	Hitterö.	Ytterby.
Silica	24·36	25·53
Yttrium earths	45·51	38·13
Cerium oxide	7·01	13·55
Ferric oxide	2·85	4·07
Ferrous oxide	11·50	7·47
Beryllium oxide	8·58	10·03
Lime	0·36	0·57
Loss on ignition	0·50	1·34
	100·67	100·51

N. H. M.

Water of Crystallisation of Alums. By J. JUTTKE (*Chem. Centr.*, 18, 777).—Potash alum, in a vacuum over sulphuric acid, loses 19 mols. H_2O, chromium alum 12—13, and iron alum, 20—21 mols. H_2O. Potash alum, heated at 100° in a current of dry air, loses 15 mols. H_2O readily, but the remainder only after prolonged heating, and breaking up of the dry crust, which retains the water. At a temperature of 20—30° potash alum gives off no water, at 42° 11 mols., at 65—91° 19 mols., and at 100° the remaining 5 mols. of water are given off. Potassium, chromium, and ammonium iron alum heated at 100° are completely dehydrated, without becoming insoluble in water, and without undergoing any decomposition. V. H. V.

Action of Hydrogen Sulphide on Cobalt Salts. By H. Baubigny (*Compt. rend.*, **105**, 751—754, and 806—809).—The action of hydrogen sulphide on solutions of cobalt salts varies, as in the case of nickel salts (Abstr., 1882, 1031), with the concentration of the solution, the nature of the acid in the salt, the ratio between the weight of acid and metal present, the ratio of free acid to the water present, the degree of saturation with hydrogen sulphide, or in other words the tension of the gas, and also with certain other conditions, including the temperature and the duration of the experiment.

Solutions of the normal sulphates of cobalt and nickel were saturated with hydrogen sulphide, and hermetically sealed in glass flasks, the liquid occupying about five-sixths of the volume of the flask. After standing for some days, precipitation is always more complete in the case of nickel than with cobalt. This, however, is only a special result. Under comparable conditions the formation of cobalt sulphide from a solution of a cobalt salt is always more rapid than the formation of nickel sulphide from the corresponding nickel salt. This is observed, for example, if the solutions saturated with hydrogen sulphide only partially fill the vessels. It follows that the tension of the gas exercises a considerable influence on the result.

Precipitation of the cobalt sulphide is prevented by the presence of free acetic acid, the proportion required to produce this result being greater the greater the concentration of the solution. More acetic acid is necessary to prevent the precipitation of cobalt than to prevent that of nickel. With sulphuric acid and similar acids, however, the differences between the two metals tend to disappear. In both cases, there is no precipitation even after several days at the ordinary temperature if the proportion of free sulphuric acid is equal to half that in combination with the metal, provided that the quantity of salt present exceeds 0·15 gram per litre. If the solutions are more dilute, some precipitation takes place, the quantity of sulphide formed being greater in the case of cobalt than in the case of nickel. The presence of the precipitated sulphide accelerates the reaction in both cases.

Rise of temperature accelerates precipitation from solutions of cobalt sulphate, but precipitation is not as complete as with nickel sulphate under the same conditions. The precipitation of nickel in fact takes place more readily than the precipitation of cobalt as the acidity of the solution increases. The more concentrated the original solution of the neutral salt, and consequently the greater the quantity of acid liberated during the reaction, the greater is the precipitation of the nickel as compared with that of cobalt. It follows that a smaller quantity of free acid is required to prevent the precipitation of cobalt than to prevent that of nickel. With weak acids, the difference is still distinct. In a solution containing only a small proportion of free acetic acid, the precipitation is greater in the case of cobalt, but if the proportion of free acid is increased the precipitation of nickel becomes the greater of the two. C. H. B.

Action of Vanadic Anhydride on Potassium Fluoride. By A. DITTE (*Compt. rend.*, **105**, 1067—1070).—When excess of vanadic anhydride is fused with potassium fluoride in a platinum crucible, care being taken to prevent access of air, a brick-red, crystalline mass is formed on cooling, and when this is treated with water, a residue of vanadic anhydride is left, and a red solution is obtained. The solution first deposits a small quantity of potassium bivanadate, formed in consequence of access of air, and then orange-red plates of the compound $3V_2O_5,2KF + 5H_2O$, which melts easily to a black liquid. The mother-liquor on further concentration deposits red, transparent prisms of the composition $4V_2O_5,2KF + 8H_2O$.

Contact with air is more completely avoided by heating the crucible at the bottom of a long glass tube. Under these conditions the aqueous solution first deposits the compound $3V_2O_5,2KF + 5H_2O$, then ruby-red prisms of the composition $3V_2O_5,2KF + 6H_2O$, and less soluble, lemon-yellow crystals of the composition $3V_2O_5,4KF$.

All these compounds are soluble in concentrated sulphuric acid, with evolution of hydrogen fluoride and formation of a red solution which becomes pale-green when diluted with much water.

When an excess of potassium fluoride is employed, the residue is pale-yellow, and on treatment with cold water first yields a saturated solution of potassium fluoride, in which the vanadium compounds are practically insoluble. A further quantity of water forms a yellow solution, which deposits small plates of the composition $2V_2O_5,2KF + 8H_2O$, and the mother-liquor when concentrated in a vacuum yields the compound $3V_2O_5,2KF + 4H_2O$. The portion of the residue least soluble in water has the composition $V_2O_5,4KF + 3H_2O$.

With a large excess of potassium fluoride, the solution yields successively large, thin, brilliant, orange-yellow lamellæ of the compound $3V_2O_5,2KF + 5H_2O$, white crystals with a greenish-yellow tinge of the compound $V_2O_5,8KF + 3H_2O$, and finally yellow crystals of the compound $V_2O_5,4KF + 2H_2O$.

If air has free access and vanadic anhydride is in excess, the residue is an orange-red mass with a vitreous fracture, and when treated with hot water some vanadic anhydride remains undissolved. The solution first deposits potassium bivanadate, and afterwards lemon-yellow crystals of the composition $V_2O_5,4KF$. Similar results are obtained with excess of potassium fluoride. Water first dissolves the excess of fluoride, and the solution obtained by further treatment deposits yellowish-white crystals of the compound $V_2O_5,8KF + 2H_2O$.

The action of potassium fluoride on vanadic anhydride yields the compounds $2V_2O_5,KF$; $3V_2O_5,2KF$; V_2O_5,KF; $3V_2O_5,4KF$; $V_2O_5,4KF$; $V_2O_5,8KF$, which may be regarded as analogous to potassium chlorochromate. Their solutions give no coloration and no precipitate with ammonia. If these compounds are regarded as derived from an oxyfluoride, the latter must be $V_2O_4F_2$. Possibly the compounds do not actually exist in the fused mass, but the aqueous solution contains several different compounds, giving rise to conditions of equilibrium in which the crystallisable salts described are formed. A solution of potassium fluoride dissolves vanadic anhydride, and the liquid deposits greenish-white crystals of the compound $V_2O_5,8KF$, which is but slightly soluble in excess of the alkaline fluoride. As the colourless solution cools it becomes yellow, and deposits lemon-yellow crystals of the compound $V_2O_5,4KF$. C. H. B.

Mineralogical Chemistry.

Metamorphic Graphite: Strata containing Garnet from the Ural Mountains. By A. KARPINSKY (*Chem. Centr.*, 1887, 821—822; from *Bull. Akad. St. Petersb.*, **31**, 484—495).—On the banks of the Bagarjak, on the eastern side of the Ural Mountains, a peculiar instance occurs of strata of graphite in limestone, thus indicating a remarkable nonconformability of the strata of the carboniferous period. In the limestone are found crinoides, in the sandstone are crystals of hornblende and quartz, together with orthoclase and plagioclase, whilst in the neighbouring village of Fadina are the usual fossils of the carboniferous period, such as stigmaria and lepidodendron. The presence of small specimens of garnet in the graphite containing strata of limestone is peculiar. An analysis of specimens gave the following results:—

SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Sp. gr.
37·12	21·31	8·82	25·83	5·72	0·94	4·065

from which the formula $3Mn_3Si_3O_{12}(Cu,Mg)_3Al_2Si_3O_{12},Fe_3Al_2Si_3O_{12}$ is deduced. The crystals were formed from twelve rhombic faces, whose apices converge in the centre of the crystal, and whose bases were of rhombic form. V. H. V.

Mineral Wax. By G. DOLLFUS and S. MEUNIER (*Compt. rend.*, **105**, 823—824).—The mineral was obtained from Sloboda Rungorska, near Kolomea, in Austrian Galicia. It occurs in petroliferous strata formed of compact non-aqueous and non-fossiliferous bluish-grey marls. It has a fibrous structure with a golden-yellow lustre, some samples strongly resembling crocidolite, whilst others resemble colophony. It melts at above 80°; sp. gr. 0·6. Boiling water does not dissolve it, and does not remove any chlorides. When placed in ether, it first becomes white and then dissolves, and if the solution is concentrated, it deposits long, colourless, monoclinic needles, which act strongly on polarised light. It imparts a yellow colour to carbon bisulphide, which gradually dissolves a considerable quantity. It is less soluble in alcohol, from which it crystallises in nacreous, white plates. The mineral has the composition C_nH_n, distils without residue, and burns with a very luminous flame. C. H. B.

Artificial Deposition of Calcite Crystals on Spicules of a Sponge. By W. J. SOLLAS (*Proc. R. Dublin Soc.*, **5**, 73).—After having been left to stand for some days in water containing an excess of calcium carbonate, some acerate and triradiate spicules of a calcisponge were found to have become incrusted with crystals of calcite. The optic axes of the calcite forming a spicule, and the crystals deposited on it, are similarly orientated. The crystals are deposited only on those regions which show the greatest liability to solution (compare Sollas, *ibid.*, **4**, 385). B. H. B.

Howlite. By S. L. Penfield and E. S. Sperry (*Amer. J. Sci.*, **34**, 220—222).—The specimen examined was obtained from the gypsum quarries at Windsor, Nova Scotia. It consisted of an egg-shaped nodule, one inch and a half in diameter, composed of microscopic flattened prisms usually broken at the ends, but occasionally terminated by two dome faces. Analysis of the air-dry powder gave the following results:—

SiO_2.	B_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	SO_3.	Total.
14·70	42·69	28·20	0·51	0·12	11·97	2·01	100·20

The mineral is thus a very acid silico-borate, having the formula $H_6Ca_2B_6SiO_{14}$. In the above analysis the boric anhydride was determined by the method suggested by F. A. Gooch (Abstr., 1887, 299), a method that was found to give most satisfactory results.

B. H. B.

Celestine and Anglesite by Senarmont's Process. By L. Bourgeois (*Compt. rend.*, **105**, 1072—1074).—Amorphous strontium and lead sulphates heated in sealed tubes at 150° with hydrochloric acid diluted with twice its volume of water are converted into crystals of celestine and anglesite respectively. Strontium sulphate is heated with an excess of acid. Lead sulphate on the other hand is employed in large excess, and the lead chloride which is formed is removed by treatment first with cold and then with boiling water.

C. H. B.

Mursinskite. By N. v. Kokscharoff (*Chem. Centr.*, 1887, 817, from *Bull. Acad. St. Petersb.*, **31**, 450—464).—This new mineral forms inclusions in topaz and is extremely scarce, sufficient material not yet having been obtained for an analysis, although it was first noticed 32 years ago. It crystallises in the tetragonal system in forms derived from a tetragonal pyramid; axial ratios $a : b : b =$ 0·56641 : 1 : 1; colour wine to honey-yellow; hardness 5—6; sp. gr. = 4·149 (?). A. J. G.

Occurrence of Harmotome in Wicklow. By J. Joly (*Proc. R. Dublin Soc.*, **5**, 165—168).—The mineral described occurs implanted on a quartz matrix in the Luganure lode, which traverses the granite of Glendalough in Co. Wicklow. The results of measurements of the crystals are in accord with those recorded by Dana, although the appearance of the crystals differs from that usually assigned to harmotome, one set of the prism faces being reduced to minute dimensions. The sp. gr. of the mineral is 2·46, and its hardness is 4·5. Before the blowpipe, it fuses without intumescence. It does not gelatinise with, but is decomposed by, hydrochloric acid. These tests confirm its identity with harmotome. No occurrence of any zeolite in Wicklow has hitherto been recorded. B. H. B.

Beryl and Iolite of Glencullen. By J. JOLY (*Proc. R. Dublin Soc.*, **5**, 48—72).—The minerals described occur in the granite of Glencullen, Co. Dublin. The beryl crystals occur in veins and bunches, and present three types: normal crystals, radiating crystals, and altered crystals. The normal beryl is of a pale apple-green colour, semitransparent to translucent. It has a sp. gr. of 2·722. Interpenetration by orthoclase is common in these crystals. The second type is remarkable in habit. The crystals radiate in a striking manner, the groups being all more or less fan-like in section. It was found by experiment that a temperature of 357° is sufficient to decolorise both green and yellow beryls in a very short time, whether in contact with air or not. With long-continued heating the temperature of alteration is possibly below 250°. The greater proportion of the total number of beryl crystals coming from Glencullen belong to the third type. The author's observations show that these crystals were primarily composed entirely of beryl, subjected to reaction with a potash felspar in a state of hot solution. They were partially replaced, the result being a variable mixture of felspar and beryl, pseudomorphous after beryl. The felspar thus mixed with the beryl is orthoclase containing iolite, a mineral as a rule foreign to Irish rocks.

The minute crystals developed through the felspar, and absent from the portions of the sections composed of beryl, appear in two forms: a wide polygonal form and a rectangular elongated form. The crystals are transparent, with uncertain dichroism. They have a pale blue colour, a vitreous lustre, a sp. gr. of 2·56, and a hardness of about 7. The fusibility is about that of iolite. On fusion, the mineral loses transparency. These characteristics clearly indicate that the small crystals are iolite. Analysis of an impure specimen gave the following results:—

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	MnO.	H_2O.	Total.
56·7	20·7	13·9	4·2	trace	trace	2·0	97·5

The formula deduced from this imperfect analysis is—

$$10SiO_2,2(Al_2O_3,FeO),MgO,H_2O.$$

B. H. B.

Studies in the Mica-group. By F W. CLARKE (*Amer. J. Sci.*, **34**, 131—137).—1. *Muscovite from Alexander Co., North Carolina.*—This mica (Analysis I) occurs at Stony Point with dolomite, iron pyrites, and rutile. All these minerals are dusted over with a dark-green chloritic coating (Analysis II), which appears to be a member of the obscure hisingerite group. A microscopical examination of the mica showed that the angle of the optic axes, measured in oil in a plane perpendicular to the plane of symmetry, is 35°.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	Na_2O.	K_2O.	F.	Ignition.	Total.
I.	45·40	1·10	33·66	2·36	1·86	1·41	8·33	0·69	5·46	100·27
II.	31·16	—	8·06	35·86	5·43	—	—	—	20·50	101·01

2. *Lepidomelane from Baltimore and Maine.*—These minerals gave on analysis the following results:—

	H_2O.	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
III.	4·48	35·78	16·39	14·55	11·02	1·08	—
IV.	4·67	32·35	17·47	24·22	13·11	1·02	0·89

	MgO.	K_2O.	Na_2O.	Total.
III.	8·67	7·76	0·56	100·29
IV.	—	0·70	6·40	100·83

III. Baltimore; formula $R'_6R''_3R'''_4Si_5O_{22}$. IV. Litchfield, Maine; formula $R'_6R''_2R'''_6Si_5O_{24}$.

These two micas and the so-called annite of Rockport (Abstr., 1887, 347), which has the formula $R'_6R''_4R'''_2Si_5O_{20}$, are built up on the same fundamental plan, and exhibit a new and highly suggestive order of variation. All the monoxide bases being united, the following general formulæ are obtained:—

Rochport........	$R'_{14}R'''_2(SiO_4)_5$.
Baltimore.......	$R'_{12}(AlO)_2R'''_2(SiO_4)_5$.
Litchfield	$R'_{10}(AlO)_4R'''_2(SiO_4)_5$.

3. *Iron-biotite from Auburn, Maine.*—In its ratios, this mica is not simple. Its formula may be approximately written—

$$R'_{11}(AlO)_3Al_2(SiO_4)_5,$$

with $R'_{11} = H_4K_2Fe_{2\frac{1}{2}}$. It seems to be a compound intermediate between the Litchfield and Baltimore micas, with R''' nearly all aluminium.

4. *Iron-mica from near Pike's Peak.*—This specimen was a bronzy-black mica, the entire core of which was made up of a soft rotten material evidently derived from the original mica. Analyses of the broad black margin of mica (V) and of the centre (VI) gave the following results:—

	H_2O.	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
V.	4·54	34·21	16·53	20·15	14·17	0·91	0·48	1·34
VI.	7·82	34·63	17·95	31·25	3·01	0·34	0·81	1·08

	Na_2O.	K_2O.	F.	Total.
V.	1·43	6·50	0·08	100·34
VI.	0·89	1·96	0·54	100·28

B. H. B.

Crocidolite from Cumberland, Rhode Island. By A. H. Chester and F. I. Cairns (*Amer. J. Sci.*, **34**, 108—111).—At Beacon Pole Hill, near the well-known mineral locality, Diamond Hill, Cumberland, Rhode Island, crocidolite occurs usually disseminated in fine particles through felspar, but often in larger, radiated nodules. Its colour is usually a dark, bluish-grey. Analysis gave the following results:—

	SiO_2.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	H_2O.	Total.
I.	52·13	15·93	21·25	—	0·22	6·26	3·95	99·74
II.	51·03	17·88	21·19	—	0·09	6·41	3·64	100·24*
III.	52·11	20·26	16·51	0·75	1·88	5·79	3·53	100·83

I and II crocidolite from Cumberland: sp. gr. 3·2; III is a new analysis of crocidolite from the Orange River, South Africa. The empirical formula suggested for crocidolite is $Fe_3Na_2H_4Fe_2Si_9O_{27}$, or $3FeO,Na_2O,2H_2O,Fe_2O_3,9SiO_2$. The authors regard crocidolite as one of the well-authenticated mineral species, and cannot agree with the conclusions of Dölter and of Kenngott (Abstr., 1886, 128), that crocidolite is merely a fibrous variety of arfvedsonite.

The mineral, named *abriachanite* by Heddle (*Min. Mag.*, **3**, 61), and the crocidolite from the Vosges Mountains, analysed by Delesse, are shown to be essentially the same substance—a magnesian variety of crocidolite. B. H. B.

Nature and Formation of Glauconite. By C. W. v. GUMBEL (*Chem. Centr.*, 1887, 813—814, from *Ber. Münch. Akad.*, 1886, 418—449).—The author has examined specimens of glauconite from different geological formations, and established their identity; specimens of this mineral from the coast of New Jersey are more particularly examined, analysis of which gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
46·9	4·06	27·09	3·6	0·2	0·7	6·16	1·28	9·25

There were present, in addition, traces of organic substances, manganese, phosphoric acid, and sulphuric acid. The author combats the view of Ehrenberg as to the suspected connection between the remnants of foraminiferæ and glauconite: it seems more probable that glauconite has been intussuscepted between the shells of the foraminiferæ. The condition of formation was probably a shallow sea, in the muddy deposits of which organisms were included, and in their decomposition gave off hydrocarbons, carbonic acid, and hydrogen sulphide. At the surface of the bubbles of gas mineral substances—such as lime, silicic acid, and, in some cases, glauconite separated, which subsequently increased by intussusception. In the ferriferous earths of Kressenberg, the nuclei of brown oxide, which is probably a metamorphic product of glauconite, has penetrated into the shells of conchylæ and echinodermata. V. H. V.

Black Marble of Kilkenny. By W. N. HARTLEY (*Proc. R. Dublin Soc.*, **5**, 486—488).—At the quarries from which this well-known marble is procured, the author noticed that the weathered surfaces of the rock exhibit a yellow-ochreous colour. This might be caused by the colour of the freshly-hewn marble being due to the presence of ferrous sulphide or of ferrous carbonate which, in presence of carbonic acid and air, become dissolved and oxidised. Fractured surfaces smelt of hydrogen sulphide, due to the existence of calcium hydrosulphide in the rock. Analysis of the marble gave the following results:—

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* This total is given as 99·94 in the original.

CO_2.	CaO.	FeO.	CuO.	MgO.	SiO_2.	H_2O.	C.	S.	Total.
40·41	55·36	0·34	0·05	0·24	1·44	0·60	1·48	0·01	99·93

B. H. B.

Analyses of Calcareous Rocks and Pozzuolana from Tevere. By Verri and Trottarelli (*Gazzetta*, **17**, 385—390).—In this paper, a series of analyses are set forth of calcareous rocks from the Tevere basin; typical specimens from the several geological periods are selected. References are also given to former memoirs in the *Reale Accademia dei Lincei* and the *Bull. Soc. Geol.*

Amongst others the following analyses of specimens of pozzuolana are of particular interest:—

	Moisture.	Organic matter.	SiO_2.	CaO.
Red pozzuolana................	3·38	4·4	44·03	2·8
Grey pozzuolana from Attighano .	2·3	3·33	59·60	2·11
Grey pozzuolana from Orte......	1·66	2·087	54·37	6·63
Maroon pozzuolana from Lerni ..	7·5	4·7	46·7	3·31

	Al_2O_3.	Fe_2O_3.	MgO.	K_2O or Na_2O.
Red pozzuolana................	30·31	9·61	1·82	3·46
Grey pozzuolana from Attighano .	30·3	6·7	0·775	3·69
Grey pozzuolana from Orte......	6·04	24·56	0·16	1·63
Maroon pozzuolana from Lerni...	13·61	20·57	9·23	3·26

V. H. V.

Serpentine of the Onondaga Salt-group at Syracuse. By G. H. Williams (*Amer. J. Sci.*, **34**, 137—145).—The eruptive nature of the matrix of the serpentine (peridotite) of Syracuse, New York, is proved from its structure, and from the inclusion of fragments of the adjacent limestone, in opposition to T. S. Hunt's theory of the aqueous origin of serpentine. Pyrope and ilmenite were not detected in the Syracuse serpentine. Chrome-iron ore and perovskite, however, are present, as was shown by an analysis of 0·0165 gram of the filtrate obtained by digesting the finely-powdered rock for a long time in concentrated hydrochloric acid under pressure, and by treating the residue with strong sulphuric acid. The analysis gave—

TiO_2.	CaO.	FeO.	Total.
34·54	12·12	54·54	101·20

B. H. B.

Peperite of the Puy de la Piquette. By F. Gonnard (*Compt. rend.*, **105**, 886—888).—The "Wacke" of the Puy de la Piquette was described by Lecoq and Bouillet as a bluish peperite of sp. gr. 2·2 to 2·3, which effervesces with an acid, and melts before the blowpipe to a brownish-black enamel. It contains fragments of basalt, highly cellular black scoria, small crystals of hornblende, calcareous nodules and crystals of mesotype, with masses of carbonised wood, the latter being covered with fibrolamellar crystals of mesotype. The calcareous nodules enclose mesotype in crystals and crystalline masses.

Apophyllite in nacreous, white, partially translucent crystals of the form *m*(110), *p*(001), *a*′(101), also occurs in the calcareous nodules, but not in the peperite itself. It occurs in small druses, and also associated with mesotype in radiating bundles, the character of which shows that the apophyllite is a later formation than the mesotype. Analcime is also present in the peperite, but not in the calcareous nodules. There are also small crystals of felspar round which, in many cases, the analcime has accumulated, and crystals of green diallage accompanied by mica. C. H. B.

An Iron of doubtful Origin. By R. B. Riggs (*Amer. J. Sci.*, **34**, 60).—This iron was found on a farm in Jefferson County, Tennessee, in a region full of small iron furnaces, whence have come a number of pseudo-meteorites. The iron is characterised by extreme hardness; its weight is 640 grams, and its sp. gr. 7·61. Analysis gave the following results:—

Fe.	Ni.	Co.	Cu.	As.	Mn.	Mg.	P.
88·27	0·76	0·19	0·03	trace	6·73	0·14	1·80

Si.	Graphite.	C.	Total.
0·15	0·86	1·46	100·39

Treated with nitric acid, the polished surfaces developed fine markings not unlike Widmanstätten figures. B. H. B.

New Meteoric Iron. By R. B. Riggs (*Amer. J. Sci.*, **34**, 59).—This meteorite was found in a collection of minerals made by the late Colonel J. J. Abert. It weighed 456 grams, and in cross-section measured 50 by 37 mm. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	S.	Graphite.	C.	Total.	Sp. gr.
92·04	7·00	0·68	0·08	0·01	0·03	0·02	99·86	7·89

In composition, therefore, it is similar to the Nelson County meteorite. B. H. B.

Aërolite from Rensselaer Co., New York. By S. C. H. Bailey (*Amer. J. Sci.*, **34**, 60—62).—In 1863 a stone of unusual appearance was found on the bank of the Tomhannock Creek in Rensselaer Co. In 1884 it was recognised as an aërolite. It weighed 1·5 kilos., with an average diameter of 10 cm. In its general aspect, upon a cut surface, it resembles the Seres, Macedonia stone. For many years this aërolite seems to have been exposed to the action of the atmosphere and of the soil without showing any deterioration. An analysis of the metallic portion of the stone gave 13·02 per cent. of metallic iron, and 3·06 per cent. of nickel. The composition of the stony portion has not yet been determined. B. H. B.

Deposition of Scorodite from Arsenical Waters in the Yellowstone Park. By A. Hague (*Amer. J. Sci.*, **34**, 171—175).—Scorodite, although a comparatively rare mineral, is found at a number of localities in the Yellowstone Park as an incrustation deposited from the water of hot springs and geysers. The best occurrence is at the Joseph's Coat Springs on Broad Creek, east of the Grand Cañon, in the form a brilliant green deposit upon the sinter. Frequently the cavities in the sinter are filled with scorodite, and occasionally it forms nodular masses half an inch in diameter. Analysis (I) of the mineral shows a nearly pure scorodite.

Other localities are Chrome Springs, and one or two places in Norris Basin. At the Constant Geyser in Norris Basin, a specimen of scorodite was analysed (II); it contained a large quantity of silica. Scorodite, as deposited from these thermal waters, is evidently a very unstable mineral. It slowly undergoes oxidation, leaving an ochreous material containing varying amounts of arsenic acid.

	Analysis III.		Analysis IV.	
	Grams per kilogram of water.	Per cent. of total material in solution.	Grams per kilogram.	Per cent. of total material in solution.
SiO_2	0·4685	28·88	0·3828	27·52
SO_3	0·0923	5·69	0·0152	1·09
CO_2	0·0155	0·95	0·0894	6·43
B_2O_3	0·0317	1·95	0·0148	1·07
As_2O_3	0·0018	0·11	0·0021	0·15
Cl	0·5740	35·39	0·4391	31·57
Br	trace	—	0·0034	0·25
H_2S	nil	—	0·0002	0·01
O (basic)	0·0185	1·14	0·0419	3·02
Fe	trace	—	trace	—
Al	0·0048	0·29	0·0009	0·06
Ca	0·0146	0·90	0·0015	0·11
Mg	0·0018	0·11	0·0006	0·04
K	0·0745	4·60	0·0267	1·92
Na	0·3190	19·67	0·3666	26·36
Li	0·0030	0·19	0·0056	0·40
Am	0·0012	0·08	0·0000	—
HCl	0·0008	0·05	—	—
Totals	1·6220	100·00	1·3908	100·00

	SiO_2.	Al_2O_3.	Fe_2O_3.	As_2O_5.	H_2O.	Total.
I.	trace	—	34·94	48·79	16·27	100·00
II.	49·83	4·74	18·00	17·37	10·62	100·56

An analysis of the water from the Constant Geyser is given (III). Its temperature was 198° F.; reaction slightly acid; sp. gr. 1·0011. For the purpose of comparison, an analysis (IV) is given of the water from the Old Faithful Geyser in the Upper Geyser Basin. Its reaction is alkaline, and sp. gr. 1·00096.

In analysis IV traces of manganese, cæsium,* and rubidium were observed. B. H. B.

Organic Chemistry.

Action of Chlorine on Amylene. By J. Kondakoff (*Chem. Centr.*, 1887, 979, from *J. Russ. Chem. Soc.*, 1887, 337).—In the course of investigations on the action of chlorine on isomeric amylenes, the author obtained from the modification insoluble in sulphuric acid, an unsaturated chloro-derivative, C_5H_9Cl, in addition to the dichloropentane $C_5H_{10}Cl_2$. From the former, two alcohols are obtainable, one a primary, boiling at 141°, and on oxidation yielding a caproic acid, the other a secondary alcohol, boiling at 117°, and yielding a ketone of boiling point 101—103°, probably methyl propyl ketone. The primary alcohol is a β-ethyl allyl alcohol, $CH_2Me{\cdot}CH{\cdot}CH{\cdot}CH_2{\cdot}OH$; the secondary alcohol differs both from methyl isopropenyl carbinol and ethyl vinyl carbinol, and probably has the constitution $CHMe{:}CH{\cdot}CHMe{\cdot}OH$. V. H. V.

Action of Hypochlorous Acid on the Hydrocarbon C_8H_{16}. By S. A. Přibytek (*Chem. Centr.*, 1887, 978, from *J. Russ. Chem. Soc.*, 1887, 338).—The hydrocarbon $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2$, obtained by Sesukoff from sodium and chlorisobutylene when treated with hypochlorous acid, yields a chlorhydrin, $C_8H_{14}(OH)_2Cl_2$, from which the dioxide $C_8H_{14}O_2$ can be obtained. The latter gives with water a tetratomic alcohol, *octylerythrol*, $C_8H_{14}(OH)_4$. V. H. V.

Ammonio-zinc Cyanides. By R. Varet (*Compt. rend.*, **105**, 1070—1072).—Pure zinc cyanide is dissolved to saturation in aqueous ammonia at a gentle heat and a current of ammonia gas is passed into the liquid, which is filtered when saturated with the cyanide, again treated with ammonia gas, and allowed to cool. A crystalline precipitate forms, but redissolves when gently heated, and separates on cooling in large, transparent, prismatic crystals of the composition $ZnCy_2,2NH_3 + H_2O$. This compound loses ammonia and water when exposed to the air, and becomes white and opaque. It is very soluble in aqueous or alcoholic ammonia, and if freshly prepared, is also soluble in water with slight decomposition, but if it has been prepared for some time, it is immediately decomposed by water. It is slowly decomposed by sodium hydroxide in the cold. When heated in a current of ammonia gas, it loses water, but no compound richer in ammonia is formed.

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* "Calcium" in the original."

When zinc cyanide is dissolved to saturation in alcohol, treated with a current of ammonia gas, and the liquid allowed to evaporate spontaneously, the compound $ZnCy_2,2NH_3$ is obtained in transparent crystals, which lose ammonia rapidly when exposed to the air and become opaque, and are very soluble in aqueous or alcoholic ammonia. The same compound is obtained by passing ammonia gas over gently heated zinc cyanide. Zinc cyanide forms only one compound with ammonia, and not a series of compounds like the chloride and bromide. C. H. B.

Methyl Mercaptan and some of its Derivatives. By J. OBERMEYER (*Ber.*, **20**, 2918—2928).—Methyl thioacetate is prepared by the action of lead methyl mercaptide on a slight excess of cooled acetic chloride; it boils at 95—96° (not 62—68°, Cahours, *Compt. rend.*, **80**, 1317, and **81**, 1163). The substance described by Cahours (*loc. cit.*) is probably a mixture of the ether with methyl iodide, acetic acid, and hydrobromic acid.

Methyl thiopropionate, C_4H_8SO, prepared from propionic chloride, is a colourless liquid of repulsive odour, boiling at 119—120°.

Methyl thiobutyrate, $C_5H_{10}SO$, is a light oil having an odour resembling that of butyric acid; it boils at 140—144°.

Methyl α-thiobenzoate, C_8H_8SO, boils at 231—232°.

Methylisopropyl sulphide, SMePr, is prepared by dissolving sodium in isopropyl mercaptan diluted with absolute ether, and the mixture, contained in a reflux apparatus, is treated with methyl iodide in small portions; it is then heated for 15 minutes in a water-bath and filtered. The heavy oil which separates from the solution when kept over night, is removed, and the ethereal solution evaporated and fractionally distilled. It boils at 93—95°.

Methyl amyl sulphide, $SMe\cdot C_5H_{11}$, is prepared by the action of methyl iodide on amyl mercaptide; it boils at 136—138°. Isoamyl disulphide is also formed.

Methyl allyl sulphide, $SMe\cdot C_3H_5$, is formed when 25 grams of lead methyl mercaptide is heated with allyl bromide and ether at 100°. It is a clear liquid of a very penetrating odour, boiling at 91—93°.

When allyl tribromide is heated with an excess of lead methyl mercaptide and ether at 100°, a compound, probably of the formula $SMe\cdot C_3H_4Br$, is obtained. It could not be purified, as it decomposes at 120—130°.

Methyl benzyl sulphide, $SMe\cdot C_7H_7$, is obtained by heating lead methyl mercaptide, and benzyl chloride at 100°. It is a clear liquid of an odour resembling horse-radish, and boils at 195—198°.

Methyl phenyl sulphide, SMe·Ph, prepared from lead thiophenol and methyl iodide, forms a clear liquid boiling at 187—188°.

Dimethyl thioresorcinol, $C_6H_4(SMe)_2$, is an oily liquid of a disagreeable odour boiling at 278°.

Methyl diphenyl sulphide, $SMe\cdot C_{12}H_9$, is obtained from lead thiodiphenyl; it crystallises from alcohol in flakes of very slender needles, melting at 107—108°.

Dimethyl diphenyl disulphide, $C_{14}H_{14}S_2$, is prepared by heating the lead mercaptide of diphenylthiohydrate with methyl iodide. It crystallises from alcohol in lustrous bright-yellow plates melting at 185—186°. N. H. M.

Brandy from a Wine from Charente Inférieure. By E. C. MORIN (*Compt. rend.*, **105**, 1019—1022).—The composition of the brandy in 100 litres is as follows:—Aldehyde, traces; ethyl alcohol, 50837 grams; normal propyl alcohol, 27·17; isobutyl alcohol, 6·52; amyl alcohol, 190·21; furfuraldehyde and bases, 2·19; fragrant oil, 7·61; acetic and butyric acids, traces; isobutylenic glycol, 2·19; glycerol, 4·38. There is no normal butyl alcohol, and amyl alcohol constitutes five-sixths of the higher alcohols. The fragrant oil is one of the constituents to which the wine owes its bouquet. (Compare Abstr., 1887, 714 and 746.) C. H. B.

Production of Normal Amyl Alcohol by the Fermentation of Glycerol by Bacillus Butylicus. By E. C. MORIN (*Compt. rend.*, **105**, 816—818).—When glycerol undergoes fermentation by *Bacillus butylicus* under the conditions determined by Fitz, 4 per cent. of the alcohols formed is normal amyl alcohol, boiling at 137—138°; refractive index at 13·5° for D = 1·414.

It is worthy of note that all the alcohols produced by *B. butylicus* are normal. C. H. B.

Action of Zinc Methyl on Valeraldehyde. By J. KUVSINOFF (*Chem. Centr.*, 1887, 987—988, from *J. Russ. Chem. Soc.*, 1887, 204). *Methyl isobutyl carbinol* is produced when zinc methyl is added to well-cooled valeraldehyde, and the product of the action decomposed with ice-water. It is a light, mobile liquid, boiling at 130°, sp. gr. 0·8271 at 0°; its *acetate* boils at 147°, sp. gr. = 0·8805 at 0°; its *ketone* boils at 116—116·5°, and on oxidation yields isopropylacetic, isobutyric, acetic, and formic acids, and is therefore identical with methyl isobutyl ketone. V. H. V.

Action of Zinc Isoamyl and Zinc Isobutyl on Aldehyde. By E. SOKOLOFF (*Chem. Centr.*, 1887, 988, from *J. Russ. Chem. Soc.*, 1887, 197—204).—When zinc isoamyl is added to aldehyde, kept cool, and the resultant product decomposed with ice-water and distilled, methyl isoamyl carbinol is obtained besides isopropylethylene, and ethyl and isoamyl alcohols. The first yields an *acetate* boiling at 166—168°, and a *ketone* boiling at 143—145°, which yields on oxidation isopropylacetic acid. Zinc isobutyl when treated in like manner yields isobutyl and ethyl alcohols. V. H. V.

Methyl Isopropenyl Carbinol. By J. KONDAKOFF (*Chem. Centr.*, 1887, 981, from *J. Russ. Chem. Soc.*, 1887, 336).—When treated with a 6 per cent. hydrochloric acid solution, methyl isopropenyl carbinol is converted into the isomeric trimethylethylene glycol. The readiness with which this change is effected is dependent on the atomic arrangement; this has also been observed in the case of unsaturated acids. V. H. V.

Iodide of Starch. By H. B. Stocks (*Chem. News*, **56**, 212—213).—The author takes exception to the four points set forth by F. Mylius (Abstr., 1887, 568), and makes the following remarks on each point. (1.) He states that iodide of starch is producd by the action of solutions of pure iodine, or of the vapour of iodine, on moist starch. (2.) That a limited amount of chlorine produces the blue colour in mixtures of hydriodic acid, or of an iodide, with starch; but that excess of chlorine destroys the colour, probably by the formation of a colourless chlorine compound of starch and iodine chloride. (3.) Silver nitrate does decolorise the iodide by removing the iodine as silver iodide, the colour being reproduced on the addition of either iodine or hydriodic acid; the action in the latter case may, however, be assumed to be due to iodine set free by the nitric acid liberated from the silver nitrate. (4.) Aqueous solutions of iodine do produce the blue colour with starch.

Water is necessary for the production of iodide of starch; therefore solutions of iodine in absolute alcohol do not colour dry starch blue. The blue iodide is destroyed by heat, the iodine being, in open vessels, partially volatilised, partially converted into hydriodic acid; in closed vessels, on the other hand, it is entirely converted into hydriodic acid. This decomposition is quick or slow according as the quantity of iodine is smaller or greater. By adding iodine to a solution decolorised in this manner, the blue colour is again formed, and this decolorisation and recolorisation may be frequently repeated with the same starch. Exposure to sunlight also decolorises iodide of starch. Iodide of starch is not affected by alcohol, ether, benzene, or carbon bisulphide; in fact, iodine may be removed from its solutions in the last two solvents by means of starch-paste.

Iodide of starch dissolves to a certain extent in water, and is precipitated from the solution by absolute alcohol, by dilute hydrochloric, sulphuric, and nitric acids, by strong hydrochloric acid, and by salts which do not react with it, such as sodium chloride. Strong nitric and strong sulphuric acid decompose it. Starch solutions are not precipitated by dilute acids like the solution of the iodide.

D. A. L.

Constituents of Rice-starch. By L. Sostegni (*Chem. Centr.*, 1887, 896, *from Stud. di Chim. Agr. di Pisa*, **6**, 48—68).—The results quoted of the amount of dextrose obtained by the saccharification of starch accord with those of Salamon. In the course of the preparation of starch cellulose by Schulze's method, a fat melting at 47—48° was extracted; the crude fatty acids obtained therefrom melt at 50—51°; the proportion of fat found was 15 to 20 per cent. of the cellulose. The portion of residue, insoluble in ether, obtained in the saccharification of starch, differs from cellulose by its solubility in a 2 per cent. solution of potash, and its partial decomposition when warmed. From its solution, acetic acid precipitates an amorphous substance, turning brown in the air, soluble in Schweizer's reagent when moist, but not when dry; it is decomposed when boiled with hydrochloric acid. The author regards starch cellulose as a mixture of cellulose with the derivatives of the latter substance or a modification of granulose. V. H. V.

Lichenin. By M. Hönig and S. Schubert (*Monatsh.*, **8**, 452—465).—As there was considerable doubt whether the carbohydrate from Iceland moss (*Cetraria islandica*) was a single substance or a mixture of two or more, the authors have reinvestigated it. The dried and sorted moss was treated repeatedly with a 1 to 2 per cent. solution of K_2CO_3. A pale-green mass quite free from the original bitter taste was thus obtained. This was then boiled for some time with water and filtered through linen. The filtrate on cooling deposited a gelatinous precipitate, which separated better when the solution was frozen. The liquid still contained some of this gelatinous substance, together with an easily soluble starch. The gelatinous precipitate, for which the authors propose to utilise the name *lichenin*, previously used for the whole extract, is very sparingly soluble in cold water, but dissolves in boiling water to an opalescent solution, which is at once cleared by the addition of a little potash. The greater part is precipitated from its solutions on cooling, or on the addition of alcohol. It is not coloured by iodine. When heated with dilute sulphuric acid, it very readily yields a crystalline dextrose, which gives a rotation $[\alpha]_j = +55\cdot52°$, and closely resembles, if it is not identical with, ordinary dextrose. The intermediate dextrin-compounds are tasteless and non-rotatory. The above-mentioned soluble carbohydrate, for which the authors propose the name *lichen-starch*, could not be obtained free from lichenin. It is strongly rotating, the rotation increasing the freer the starch is from lichenin. It is easily soluble in water, but is thrown down as a flocculent precipitate by alcohol. The highest rotation obtained was $[\alpha]_j = +102\cdot82°$. It is coloured blue by iodine. Diastase converts it readily into a dextrin showing rotation $[\alpha]_j = 162\cdot44°$. Lichenin is not affected by diastase. Lichen-starch, therefore, appears to be a soluble, unorganised modification of ordinary starch. L. T. T.

Reactions of Chloral. By O. Rebuffat (*Gazzetta*, **17**, 406—409).—Chloral and sodium acetate, in presence of acetic anhydride, do not react in accordance with Perkin's reaction; the change is for the most part more profound, leading to the destruction of the molecule of chloral. Sodium acetate at a low temperature combines directly in equimolecular proportions with sodium acetate to form a compound, $C_2Cl_3HO,C_2H_3O_2Na$, which is white and minutely crystalline; it is decomposed by water and by alcohol to form chloral alcoholate. Experiments were also made with the anhydrides of other fatty acids, but without success. V. H. V.

Trithioacetaldehydes. By W. Marckwald (*Ber.*, **20**, 2817—2818; compare Abstr., 1886, 864).—γ-Trithioacetaldehyde, when mixed with four times its weight of ethyl iodide and allowed to remain in a closed vessel for some weeks, suddenly undergoes conversion into a crystalline mass of the β-derivative. This change is not due to the presence of free iodine in the ethyl iodide, since the change does not take place when an ethereal solution of the γ-aldehyde containing a small quantity of iodine is similarly treated. W. P. W.

Metallic Derivatives of Acetylacetone. By A. COMBES (*Compt. rend.*, **105**, 868—871).—The author has previously shown that acetylacetone has the constitution $CH_2Ac{\cdot}COMe$, and that the hydrogen of the CH_2-group is readily displaced by chlorine or by sodium.

Acetylacetone and its homologues act on metallic salts like true acids, and yield a new series of crystalline compounds of the general formula $M(C_5H_7O_2)_n$, in which M is a metal with a valency *n*. The sodium and potassium derivatives form white, hexagonal prisms belonging to the rhombic system, and are most readily obtained by adding the required quantity of sodium or potassium ethoxide to an alcoholic solution of acetylacetone. They are somewhat soluble in absolute alcohol, but are insoluble in ether.

The magnesium salt is obtained by mixing acetylacetone with an excess of magnesium carbonate. There is rapid effervescence, and the filtered liquid when evaporated in a vacuum, deposits transparent, colourless, hexagonal prisms belonging to the rhombic system, which are anhydrous when dried at 125°. The aluminium compound is formed in the preparation of acetylacetone, and is also obtained by the action of the latter compound on a slightly acid solution of aluminium chloride. It is insoluble in water, somewhat soluble in alcohol, but less soluble in ether. When the solution is concentrated, it deposits nacreous crystals of the same form as the preceding compound, but they are readily decomposed by heat.

The copper salt is obtained in pale blue needles of the same form, when a somewhat concentrated solution of cupric acetate is mixed with a warm saturated aqueous solution of acetylacetone. The compound is insoluble in water, and in moderately dilute solutions the precipitation of the copper is complete. Larger crystals are formed when a dilute solution of cupric chloride is added to a boiling solution of acetylacetone. The crystals are anhydrous when dried at 125°.

Ferric chloride and acetylacetone yield a dark-red solution, the formation of which may be used as a test for the ketone, and when this is extracted with ether the red compound is dissolved. When the ether evaporates, the iron salt is deposited in bright-red crystals, similar in form to those of the ammonium salt.

The lead salt is formed by the action of lead carbonate on the ketone, is soluble in water, and resembles the magnesium compound in its crystalline form.

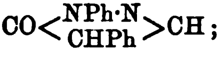
Acetylacetone behaves in fact like a monobasic acid. The sodium and potassium salts are, however, decomposed by hot water, with formation of acetone and an alkaline acetate, and the aluminum and iron compounds are not decomposed by ammonia in alcoholic solution. The sodium salt and methyl iodide yield a new derivative, *methylacetylacetone*, boiling at 165°, which has acid properties similar to those of the original compound. It seems, in fact, that the group $\cdot CO{\cdot}CH_2{\cdot}CO\cdot$ has the properties which characterise the group COOH, except that the two hydrogen-atoms cannot act successively. Salts of the type $C_5H_6O_2M$, in which M is a bivalent metal, have not yet been obtained, but the homologues of acetylacetone form salts of the type $(C_5H_6RO_2)_nM$, in which R is an alkyl radicle, and M is a metal of valency *n*. C. H. B.

Preparation of α-Bromo-acids. By J. VOLHARD (*Annalen*, **241**, 141—163).—Very good yields of α-brominated acids may be obtained by a slight modification of Hell's process (Abstr., 1881, 711). The action of the bromine and phosphorus on the acid, or preferably the crude anhydride, is carried on in a flask provided with a reflux condenser, instead of in sealed tubes. The bromine and the other ingredients must be free from moisture. The bromide is slowly dropped into boiling water, in order to convert it into the monobrominated acid. The following compounds were prepared: *α-monobromosuccinic acid* forms four-sided prisms, and melts at 159°. The *ethyl* salt boils at 150—160° under 50 mm. pressure, and the *methyl* salt at 132—136° under 30 mm. pressure. α-Monobromosuccinic acid is decomposed by boiling with water, yielding fumaric acid. *α-Bromopropionic acid* forms prismatic crystals melting at 24·5°, and *α-bromisovaleric acid* melts at 40°, and distils at 230° with slight decomposition.

W. C. W.

Ethereal Salts of Aldehydo-acids. By W. WISLICENUS (*Ber.*, **20**, 2930—2934).—When a mixture of ethyl acetate and ethyl formate is added by drops to twice the amount of ether in which sodium is placed, and the product decomposed by dilute sulphuric acid, an oil is obtained which gives an intense blue-violet colour with ferric chloride, and reacts with phenylhydrazine. The compound is probably *ethyl formylacetate*, COH·CH$_2$·COOEt. It could not be purified; when kept in a desiccator, crystals of ethyl trimesate melting at 133°, separate. The yield of the latter is better than that obtained by Piutti's method (Abstr., 1887, 491).

Ethyl phenylformylacetate, COH·CHPh·COOEt, is prepared by suspending dry sodium ethoxide in absolute ether (3 parts), adding a mixture of ethyl phenylacetate and ethyl formate, and keeping the whole for several days in a closed vessel. The product is shaken with water, being kept cold with ice, and the aqueous solution is treated with sulphuric acid and extracted with ether. The ethereal extract is washed with soda, filtered, and freed from ether in a vacuum. The residue, consisting of a crystalline substance and an oil, is filtered, and the oil distilled in a vacuum. It boils at 144—145° under 16 mm. pressure. When boiled with dilute aqueous soda, it is decomposed into phenylacetic and formic acids; the free acid could not be obtained. The alcoholic solution of the ethereal salt gives a very intense blue-violet coloration with ferric chloride. It reacts readily with phenylhydrazine, with formation of the *compound*



$$CO{<}\begin{matrix}NPh{\cdot}N\\CHPh\end{matrix}{>}CH;$$

this crystallises in plates melting at 195—196°, and is soluble in alkali, sparingly soluble in ether.

The crystalline compound obtained in the preparation of ethyl phenylformylacetate is readily purified by crystallisation from ether; it has the same composition as ethyl phenylformylacetate; it gives no colour reaction with ferric chloride. The liquid isomeride changes slowly at the ordinary temperature into the crystalline compound, but the change is immediate at the melting point of the crystals, 69—71°. The crystalline compound is also decomposed by alkali into formic and phenylacetic acids.

Ethyl methylformylacetate, COH·CHMe·COOEt, is a colourless oil, of agreeable odour, and boils at 160—162°; it gives an intense red-violet coloration with ferric chloride, and yields a pyrazoline-derivative with phenylhydrazine.

The above ethereal salts are derivatives of the half-aldehyde of malonic acid which v. Pechmann assumed (*Ber.*, **17**, 936) to exist as an intermediate product in the synthesis of cumalinic acid.

N. H. M.

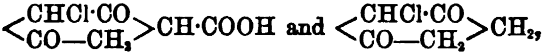
Conversion of Benzene-derivatives into Fatty Compounds by the Action of Chlorine in Alkaline Solution. By A. HANTZSCH (*Ber.*, **20**, 2780—2795).—When phenol (at most 50 grams) is dissolved in a moderate excess of aqueous soda (sp. gr. = 1·12), and the solution, after dilution with 2 to 3 times its volume of water, is treated at 0° with chlorine, the colour changes through green to brown, and a liquid or semi-solid brown mass separates; this dissolves on the addition of more alkali, but subsequently the solution slowly deposits a grey or black powder insoluble in alkali, and finally by alternating the addition of chlorine and alkali a point is reached, indicated by the dull-yellow colour of the solution, beyond which chlorination must not be carried. After precipitation of trichlorophenol by hydrochloric acid, a compound, *trichlorodihydroxyamenylcarboxylic acid*, $C_6H_5Cl_3O_4$, is extracted by ether from this solution, and is obtained by cautious evaporation of the ether as an oil, which is best purified by heating it with aqueous ammonia, recrystallising the ammonium salt, decomposing this with sulphuric acid, extracting with ether, and repeatedly recrystallising from water. The acid crystallises in slender, white needles, which are anhydrous, and melt at 176—177° with complete decomposition; once, however, large, efflorescent, seemingly monoclinic crystals containing 4 mols. H_2O were obtained. It has a sour and yet distinctly sweet taste, is unaltered by exposure to the air, dissolves readily in water, alcohol, and ether, and when boiled in aqueous solution decomposes with evolution of hydrogen chloride. Under the conditions given, the yield of the acid was 50 per cent. The acid is monobasic, and the *ammonium* salt, $C_6H_4Cl_3O_4·NH_4 + 2H_2O$, is the most characteristic compound; this crystallises in lustrous, rhombic prisms, has a neutral reaction and very sweet taste, is sparingly soluble in water with partial decomposition, and is not rendered anhydrous by exposure over sulphuric acid or by heating; it decomposes at 123°. The remaining salts are readily soluble with the exception of the *mercurous* salt, which crystallises in stellate groups of needles, and is converted into a dense, white, microcrystalline powder by heating with water. Concentrated alcoholic potash completely decomposes the acid with the formation of chloride and carbonate. The *methyl* salt, $C_6H_4Cl_3O_4Me$ crystallises in needles, melts at 126°, and is insoluble in water. The acid does not form derivatives with hydroxylamine and phenylhydrazine, but yields with acetic anhydride a *diacetyl*-derivative, $C_6H_3Cl_3O_4Ac_2$, which crystallises best from acetic acid, melts at 188—192° with complete decomposition, and is insoluble in cold water.

When the acid, or better its ammonium salt, is treated with zinc-dust and ammonia, or preferably with sodium-amalgam, and the product after acidification is extracted with ether, *dichlorodihydroxyamenylcarboxylic acid*, $C_6H_3Cl_2(OH)_2\cdot COOH$, is obtained. This very closely resembles the trichloro-acid, and melts at 176—177°; it differs from it, however, by readily crystallising in large, lustrous prisms, by yielding an ammonium salt which does not crystallise well and melts at 185°, and by forming an *acetyl*-derivative melting at 132—134°. Concentrated aqueous soda converts the acid into a *sodium* salt, $C_6H_3ClO_4Na_2 + 6H_2O$, crystallising in canary-yellow needles. The corresponding acid could not be isolated, but salts were prepared, and these, with the exception of the copper salt which is green, are yellow. The sodium salt gives with ferric chloride a brownish-yellow precipitate, which dissolves in excess of the reagent to a dark-green solution. The salt is unstable and decomposes on heating with water, the solution becoming alkaline, whilst mineral acids, even in the cold, destroy its colour, and convert it, with the evolution of carbonic anhydride, into a white, microcrystalline acid of the composition $C_5H_5ClO_2$. This substance is very unstable; it melts at 96—97° with complete decomposition into a carbonaceous mass, and is sparingly soluble in water, soluble in alcohol and ether, yielding solutions from which, with the exception of the last, the compound cannot again be obtained by crystallisation. The salts are intensely coloured; the *sodium* salt, $C_5H_4ClO_2Na + 3H_2O$, which can also be obtained from dichlorodihydroxyamenylcarboxylic acid by heating with concentrated aqueous soda at 100°, is readily soluble in water, very sparingly soluble in excess of aqueous soda, and crystallises in scales.

With regard to the constitution of these derivatives, the formula $CH_2Cl\cdot C(OH)\vdots CCl\cdot C(OH)\vdots CCl\cdot COOH$ is ascribed to the compound $C_6H_5Cl_3O_4$, termed trichlorodihydroxyamenylcarboxylic acid. In support of this view, it is urged that, together with the acid, the symmetrical trichlorophenol [OH : Cl : Cl : Cl = 1 : 2 : 4 : 6] is always obtained, and that the acid can be readily prepared from this trichlorophenol under conditions similar to those employed in the case of phenol, 10 grams of trichlorophenol yielding 7 grams of the ammonium salt of the acid. It is probable, therefore, that the further action of chlorine in alkaline solution causes the benzene-ring in trichlorophenol to break at the point 1 : 2 or 1 : 6. To dichlorodihydroxyamenylcarboxylic acid is assigned the constitution

$$CH_2Cl\cdot C(OH)\vdots CCl\cdot C(OH)\vdots CH\cdot COOH.$$

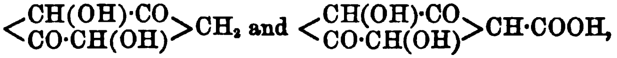
The compound $C_6H_5ClO_4$ derived from it is the carboxylic acid of the compound $C_5H_5ClO_2$, which despite its acid character is not a true acid, since it does not yield an ethyl salt either by treatment in alcoholic solution with hydrogen chloride, or by the action of ethyl iodide on its sodium salt. With bromine, it does not form additive but only substitution derivatives; ammoniacal silver nitrate and cuprous chloride are not precipitated by it, and its sodium salt, when treated with phenylhydrazine acetate, yields an amorphous *phenylhydrazide*, whose composition approximates to that required by the formula $C_5H_6Cl(N_2PhH)_2$. The formulæ



$$<\begin{matrix}\mathrm{CHCl\cdot CO}\\ \mathrm{CO{-}CH_2}\end{matrix}>\mathrm{CH\cdot COOH} \text{ and } <\begin{matrix}\mathrm{CHCl\cdot CO}\\ \mathrm{CO{-}CH_2}\end{matrix}>\mathrm{CH_2},$$

are ascribed to the two compounds, which are termed *chlorodiketopentamethylenecarboxylic acid* and *chlorodiketopentamethylene* respectively, and the analogy between these and derivatives of the similarly constituted diketohexamethylene-derivatives is pointed out in the paper.

It has not been found possible as yet to displace the remaining chlorine-atom in chlorodiketopentamethylene, but it is possible to simultaneously withdraw all the chlorine from trichlorodihydroxyamenylcarboxylic acid. When the acid, or preferably its ammonium salt, is treated with a considerable excess of concentrated baryta-water, and heated to about 60°, *barium dihydroxydiketopentamethylenecarboxylate*, $C_6H_2O_6Ba_2 + 4H_2O$, separates as a bright-yellow powder, insoluble in water. This salt effervesces on the addition of acetic acid, and is converted into the *barium* salt of *dihydroxydiketopentamethylene*, $C_5H_4O_4Ba + 3\frac{1}{2}H_2O$, which very closely resembles the preceding salt. Dihydroxydiketopentamethylene could not be prepared in the pure state; it is obtained as a yellow oil from the barium salt by treating it with hydrochloric acid and extracting with ether, and shows at first a tendency to crystallise, but very rapidly decomposes. It dissolves readily in water, reduces silver nitrate, and yields a compound with phenylhydrazine. The formulæ



$$<\begin{matrix}\mathrm{CH(OH)\cdot CO}\\ \mathrm{CO\cdot CH(OH)}\end{matrix}>\mathrm{CH_2} \text{ and } <\begin{matrix}\mathrm{CH(OH)\cdot CO}\\ \mathrm{CO\cdot CH(OH)}\end{matrix}>\mathrm{CH\cdot COOH},$$

are assigned to dihydroxydiketopentamethylene and its carboxylic acid respectively.

Trichlorophloroglucinol on treatment with baryta yields neither the trichloro-acid nor any of its decomposition products, whilst phloroglucinol and the three dihydroxybenzenes, when treated in a similar manner to phenol, do not yield crystalline ammonium salts, but only acid syrups, which on reduction with zinc-dust and ammonia give monochloracetic acid in large quantity, but no dichlorodihydroxyamenylcarboxylic acid.

Bromine, under precisely similar conditions to the above, does not act on phenol further than to produce tribromophenol.

W. P. W.

Derivatives of Isosuccinic Acid. By G. KÖRNER and A. MENOZZI (*Gazzetta*, **17**, 425—441).—In continuation of a former paper on α-amido-isosuccinic acid, or α-isoaspartic acid (Abstr., 1887, 801), the salts are more fully described. The sodium salt, $C_4H_6NO_4Na$, crystallises either in needles with 1 mol. H_2O from concentrated solutions, or in prisms with 4 mols. H_2O in large, transparent prisms. The potassium salt is anhydrous. The calcium, magnesium, zinc, cadmium, lead, copper, and silver salts are described, as also the compounds it forms with hydrochloric and nitric acids. The *methyl* salt, formed from methyl iodide and the silver salt, crystallises in white needles; when the potassium salt is heated with methyl iodide, the *betaïne potassio-iodide*, $C_4H_3NMe_3O_4K_2I,7H_2O$, is produced; it is very hygroscopic, and forms an *aurochloride*, $C_4H_5NMe_3ClO_4,AuCl_3$, a yellow, insoluble precipitate.

Amido-α-isosuccinamic acid, or *α-isoasparagine*,

$$NH_2{\cdot}CMe(CONH_2){\cdot}COOH,$$

obtained by heating the neutral amide with aqueous ammonia in sealed tubes, forms crystals with hexagonal base, more soluble in cold than in hot water; it forms a *copper* salt, $(C_4H_7N_2O_3)_2Cu$, crystallising in small tables.

Amido-α-isosuccinamide, $NH_2{\cdot}CMe(CONH_2)_2$, obtained by heating pyruvic and hydrocyanic acids, and treating the resultant product with alcoholic ammonia, crystallises in tables with a rhombic base, sparingly soluble in cold, readily in hot water. When boiled with barium or potassium hydroxides it gives for each molecule two molecules of ammonia; it is decomposed only to a slight extent by magnesia. Its *hydrochloride*, *sulphate*, and *nitrate* crystallise in prisms, and are very soluble in water. V. H. V.

Oxidation of Copaiba Balsam. By S. LEVY and P. ENGLÄNDER (*Annalen*, **242**, 189—214).—The most important facts contained in this paper have already appeared in this Journal (Abstr., 1886, 250). The unsymmetrical dimethylsuccinic acid obtained by the oxidation of copaiba balsam is identical with the acid described by Barnstein (this vol., p. 135). The acid forms triclinic crystals [$a : b : c = 2{\cdot}0294 : 1 : 1{\cdot}1909$; $\alpha = 118° 36'$, $\beta = 95° 16'$, $\gamma = 101°$]. The barium salt, $C_6H_8O_4Ba + 2\frac{1}{2}H_2O$, is monoclinic [$a : b : c = 1{\cdot}6006 : 1 : 1{\cdot}709$; $\beta = 97° 26'$]. The salts of calcium, $C_6H_8O_4Ca + H_2O$, and ammonium, $C_6H_8O_4(NH_4)_2$ and $C_6H_9O_4{\cdot}NH_4$, are crystalline. The normal sodium salt, $C_6H_8O_4Na_2 + 11H_2O$, forms silky prisms, and the acid salt, $C_6H_9O_4Na + 3\frac{1}{2}H_2O$, monoclinic prisms,

$$a : b : c = 1{\cdot}83653 : 1 : 4{\cdot}18006;\ \beta = 90° 43'.$$

The anhydride of dimethylsuccinic acid melts at 29°. It unites with phenylhydrazine, forming dimethylsuccinylphenylhydrazine, a compound crystallising in monoclinic plates [$a : b : c = 1{\cdot}05521 : 1 : 0{\cdot}82996$; $\beta = 99° 57'$]. It melts at 131—132°. The imide of dimethylsuccinic acid melts at 106°. W. C. W.

Dibromosebacic Acid and some of its Derivatives. By A. CLAUS and T. STEINKAULER (*Ber.*, **20**, 2882—2889).—*Dibromosebacic acid*, $C_{10}H_{16}Br_2O_4$, is prepared by heating sebacic acid and bromine ($2\frac{1}{2}$ mols.) at 160—170° for about three hours. The oily product solidifies after some hours to a crystalline mass which is freed from adherent oil by suction on porous plates. It crystallises from water in long, feathery needles melting at 115° (uncorr.), and is readily soluble in alcohol, ether, chloroform, and benzene, sparingly soluble in boiling water. Prolonged boiling with water decomposes the acid and its salts with elimination of hydrobromic acid. Sulphuric acid dissolves it unchanged. The *sodium salt*, $C_{10}H_{14}Br_2O_4Na_2$, is a heavy white, crystalline substance, very readily soluble in water, from which it crystallises with 3 mols. H_2O. The *hydrogen potassium salt* is almost insoluble in cold water; the *barium* (with 2 mols. H_2O), *calcium* (with 2 mols. H_2O), *lead*, *silver*, *copper*, and *ammonium salts* were also prepared. The *methyl salt* crystallises in small, lustrous, rhombohedric plates melting at 50° (uncorr.); the *ethyl salt* is a thin oil.

Hydroxysebaceïc acid, $C_{10}H_{18}O_5$, is prepared by boiling sodium dibromosebate with water, evaporating to dryness on a water-bath, digesting over sulphuric acid, and extracting with absolute alcohol. The filtrate is neutralised with alcoholic soda. The sodium salt so obtained is converted into the insoluble lead salt which is then decomposed with hydrogen sulphide. The acid is readily soluble in hot water and in cold alcohol, from which it separates in small crystalline grains melting at 143° (uncorr.); it is very sparingly soluble in ether, insoluble in benzene and chloroform. The *sodium salt*, $C_{10}H_{14}O_5Na_2$, forms a white, sandy powder very readily soluble in water.

Dihydroxysebacic acid, $C_{10}H_{18}O_6$, is obtained by boiling an aqueous solution of dibromosebacic acid with freshly precipitated silver oxide; the product is filtered, treated with hydrogen sulphide, and evaporated to a syrup; this becomes crystalline when kept over sulphuric acid. It is very readily soluble in water, alcohol, and glacial acetic acid, sparingly soluble in ether, insoluble in benzene and chloroform; it melts at 130° (uncorr.) and is decomposed at a higher temperature. It is optically inactive. The *sodium salt*, $C_{10}H_{16}O_6Na_2$, is very soluble in water.

N. H. M.

Constitution of Levulinic and Maleïc Acids. By A. Michael (*Amer. Chem. J.*, **9**, 364—372).—The reactions brought forward by Anschütz (Abstr., 1887, 916) in favour of the new constitutional formulæ suggested by Roser for maleïc and levulinic acids are examined. It is shown that by assuming certain reactions for ketones or for aldehydes similar in kind to those already known, the syntheses and transformations of these two acids and also of several others such as their acetyl-derivatives, mucobromic acid, the dibromosuccinic acids, &c., are quite as easily explained by the old formulæ as by the new ones of Roser.

H. B.

Butenyltricarboxylic and Ethylsuccinic Acids. By G. Polko *Annalen*, **242**, 113—126).—*Ethyl butenyltricarboxylate*,

$$CH_2Me{\cdot}CH(COOEt){\cdot}CH(COOEt)_2,$$

is prepared by adding 48 grams of ethyl malonate to a warm solution of 6·9 grams of sodium in 77 grams of alcohol; 48·5 grams of ethyl α-bromobutyrate is added to the product. It is a pale-yellow liquid boiling between 271° and 281°. Its sp. gr. is 1·065 compared with water at 17°. The free acid is soluble in water, alcohol, ether, and acetone. It melts at 119°, and begins to decompose at 124°. The barium salt, $Ba_3(C_7H_7O_6)_2$, and silver salt, $Ag_3C_7H_7O_6 + 1\frac{1}{2}H_2O$, are amorphous. The normal calcium salt, $Ca_3(C_7H_7O_6)_2$, is very hygroscopic. The acid salts, $CaH_4(C_7H_7O_6)_2$ and $CaH(C_7H_7O_6) + 2\frac{1}{2}H_2O$, are crystalline and insoluble in alcohol. The zinc, strontium, and potassium salts are amorphous.

Ethylsuccinic acid, COOH·CHEt·CH_2·COOH, is prepared by distilling butenyltricarboxylic acid. It is also formed in the saponification of ethyl butenyltricarboxylate. It melts at 97° and is identical with the α-ethylsuccinic acid described by Huggenberg (Abstr., 1878, 782). In addition to the salts described by Huggenberg, the crystalline strontium salt and the methyl salt were prepared. The latter boils at 202—205°. The anhydride remains liquid at −19°. Its sp. gr. at 34° is 1·165. The amide melts at 214° with decomposition. It is insoluble in cold water and in alcohol. W. C. W.

Isobutenyltricarboxylic Acid and Unsymmetrical Dimethylsuccinic Acid. By F. Barnstein (*Annalen*, **242**, 126—140).—*Ethyl isobutenyltricarboxylate*, COOEt·CMe_2·CH$(COOEt)_2$, is prepared by the action of ethyl α-bromisobutyrate on ethyl sodiomalonate in alcoholic solution. It boils at 272—275°, and its sp. gr. is 1·064 compared with water at 17°. The free acid is difficult to obtain in the crystalline state. It is soluble in water, alcohol, ether, and acetone. On boiling the aqueous solution, carbonic anhydride is evolved. The acid melts at 120° with decomposition, yielding unsymmetrical dimethylsuccinic acid. The sodium, magnesium, barium and silver salts of isobutenyltricarboxylic acid are amorphous. The potassium salt, $K_3C_7H_7O_6 + 2H_2O$, forms efflorescent prisms. The calcium salts, $Ca_3(C_7H_7O_6)_2 + 9H_2O$ and $Ca(C_7H_7O_6)_2 + 2H_2O$, are crystalline.

Unsymmetrical dimethylsuccinic acid, COOH·CMe_2·CH_2·COOH, melts at 139°, and is freely soluble in alcohol, ether, acetone, and in hot water. It forms acid and normal salts. The normal salts of the heavy metals and alkaline earths are, as a rule, very sparingly soluble in water. The normal potassium salt is amorphous and deliquescent; the acid salt, $C_6H_9O_4K + 5H_2O$, crystallises in plates which effloresce on exposure to the air. The normal barium salt, $C_6H_8O_4Ba + 2H_2O$, is crystalline; the acid salt is also crystalline, and readily soluble in water. The cadmium salt, $C_6H_8O_4Cd + 6H_2O$, and the lead salt, $C_6H_8O_4Pb + H_2O$, are crystalline, and dissolve with difficulty in water. *Dimethylsuccinyl chloride*, $C_6H_8O_2Cl_2$, boils at 200—202°. *Diethyl dimethylsuccinate* boils at 213—215°. Its sp. gr. at 17° is 1·0134 compared with water at the same temperature. The *dimethyl salt* boils at 200°; sp. gr. 1·0568 at 16°. *Dimethylsuccinic anhydride* boils at 215°. Thiophen-derivatives cannot be obtained by the action of phosphorus sulphide on unsymmetrical dimethylsuccinic acid. W. C. W.

Furfuran Derivatives. By W. Marckwald (*Ber.*, **20**, 2811—2817; compare Abstr., 1876, ii, 444).—Furfuracrylic acid is best obtained by heating furfuraldehyde (1 part), sodium acetate (2 parts), and acetic anhydride (2 parts) at 250° for 11 hours; the yield amounts to more than 80 per cent. of that theoretically possible. The ammonium salt of its reduction-product, furfuropropionic acid, is converted into *furfuropropionamide*, $C_6H_7O{\cdot}CONH_2$, by heating for several hours in a closed tube at 220°; this crystallises in white needles, melts at 98°, distils at 270° without decomposition, is soluble in water, alcohol, ether, and benzene, sparingly soluble in light petroleum, and on treatment with bromine and aqueous potash does not yield the corresponding amine, since the furfuran nucleus alone is attacked. When furfuracrylic acid (1 part) is heated with 95 per cent. alcohol (3·5 parts) and saturated with hydrogen chloride, the ethyl salt of a bibasic acid, $C_5H_8O(COOEt)_2$, is obtained as an oil which distils at 286°; this is heavier than and insoluble in water, soluble in alcohol and ether in all proportions, and has a pleasant, aromatic odour and a very bitter taste; the yield amounts to more than 80 per cent. of that theoretically possible. When saponified, it yields the corresponding *acid*, $C_7H_{10}O_5$, which crystallises from water in large, colourless, transparent, thin prisms, melts at 138°, or with partial decomposition at about 110° when heated for some time in an open vessel, and has a very bitter taste. On distillation, it is converted into oily decomposition-products of partly acid and partly neutral character. The *barium*, *calcium*, *zinc*, and *copper* salts were prepared; the silver salt, $C_7H_8O_5Ag_2$, forms microscopic needles. Since the ethyl salt yields a *phenylhydrazide*,

$$C_{11}H_{18}O_4 : N{\cdot}NHPh,$$

the author ascribes to the acid the formula

$$COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

and adduces the following evidence in its support; the acid is not reduced by sodium amalgam, does not form an additive compound with bromine, and on oxidation with dilute nitric acid is converted into succinic acid (the yield amounting to more than 40 per cent. of the acid employed), and a liquid fatty acid (? acetic or propionic acid). The acid is not acted on when heated at 200° with hydriodic acid saturated at 0°, whilst addition of amorphous phosphorus leads to experimental difficulties which have not yet been surmounted.

W. P. W.

Action of Nitric Acid on Symmetrical Trichlorobenzene. By C. L. JACKSON and J. F. WING (*Amer. Chem. J.*, **9**, 348—355).—In proving the constitution of benzenetrisulphonic acid (this vol., p. 152), it was found that with fuming nitric acid, symmetrical trichlorobenzene did not yield a mononitro-derivative melting at 68° (Beilstein and Kurbatow, *Annalen*, **192**, 233), but the dinitro-derivative melting at 130°. If sulphuric acid was used at the same time, the trinitro-derivative was obtained. Whether a mono-, di-, or tri-nitro-compound is obtained depends not only on the temperature and presence or absence of sulphuric acid, but also to a very considerable extent on the purity of the acid employed, an acid of sp. gr. 1·51, free from nitrogen peroxide, being more effective than one of sp. gr. 1·534 containing much nitrogen peroxide.

Trichlorobenzene (1 : 3 : 5) is best formed by the chlorination of dichloraniline prepared by Witt's method (this Journal, 1876, i, 264). *Trichlorodinitrobenzene*, $C_6HCl_3(NO_2)_2$, is produced at the ordinary temperature by the action of nitric acid of sp. gr. 1·505 on trichlorobenzene. It crystallises from alcohol in white prisms melting at 129·5°. The mononitro-compound is readily obtained by boiling with nitric acid of sp. gr. 1·46. *Trichlorotrinitrobenzene*, $C_6Cl_3(NO_2)_3$, is prepared by using a mixture of fuming sulphuric acid and nitric acid of sp. gr. 1·505. It crystallises from alcohol in nearly white needles melting at 187°. H. B.

Action of Sulphuric Acid on Bromodurene. By O. JACOBSEN (*Ber.*, **20**, 2837—2840).—When bromodurene is treated with eight times its weight of sulphuric acid at the ordinary temperature, and the mixture allowed to remain for 10 to 12 days, a thick brown liquid is obtained, which, on the addition of ice and subsequently of water, yields a residue consisting chiefly of dibromodurene, together with hexamethylbenzene and unaltered bromodurene. The aqueous solution was free from halogenated sulphonic acids, but contained at least three sulphonic acids, one of which on hydrolysis yields prehnitene, whilst the other two yield pseudocumene. From these results, the author concludes that sulphuric acid acts in this case as a bromine-carrier, converting the bromodurene into dibromodurene and durene (compare Neumann, Abstr., 1887, 573), the latter of which in the presence of sulphuric acid yields pseudocumene, prehnitene, and hexamethylbenzene in the manner already described by him (Abstr., 1887, 660).

Dibromodurene, under similar conditions, is not acted on by sulphuric acid.

Probably sulphuric acid acts as a bromine-carrier when in its presence bromobenzene and paradibromobenzene are converted into dibromobenzenesulphonic acid and a mixture of tetra- and hexabromobenzene respectively, as observed by Herzig (Abstr., 1882, 46). The author has also found that dibromometaxylene, [Me : Me : Br : Br = 1 : 3 : 4 : 6], when treated with chlorosulphonic acid, yields the chloride of its sulphonic acid together with a considerable quantity of tetrabromometaxylene, although but a small quantity of the latter results when the same dibromometaxylene is heated with sulphuric acid at 240°, an isomeric liquid dibromometaxylene being the chief product in this case. W. P. W.

Aniline Salts. By A. DITTE (*Compt. rend.*, **105**, 813—816).—*Aniline molybdate*, $2NH_2Ph,3MoO_3,5H_2O$, forms hard, brilliant, transparent, prismatic crystals, which lose water when gently heated, and decompose at a higher temperature. It is obtained by mixing a warm concentrated solution of ammonium molybdate with excess of a concentrated solution of aniline hydrochloride. Oily drops separate and rapidly change to a crystalline precipitate, and when this is dissolved in hot water and the solution cooled, the salt crystallises in radiating groups.

Aniline tungstate, $2NH_2Ph,4WoO_3,3H_2O$, analogous to ammonium metatungstate, forms long, brilliant, transparent needles, which lose water when gently heated, and at a higher temperature burn with a smoky flame leaving a residue of tungstic anhydride. When ammonium tungstate is mixed with a boiling solution of aniline hydrochloride, no reaction takes place, but if aniline is added, a portion of it dissolves, and when the still acid liquid is concentrated and cooled, the aniline tungstate crystallises.

Three aniline vanadates can be obtained. Warm solutions of ammonium vanadate and aniline hydrochloride yield a red liquid, acid to litmus; when this is cooled, it deposits yellow needles of the composition $NH_2Ph,V_2O_5,4H_2O$, which darken on exposure to light, and at 100° lose water and become green with a metallic lustre. At a higher temperature, the salt blackens and decomposes. If a small quantity of aniline is added to the mixed solutions in the experiment just described, and the black precipitate which forms filtered off, a reddish-brown liquid is obtained, which after some hours deposits brilliant, reddish-brown needles of the composition $4PhNH_2,3V_2O_5,18H_2O$. They lose water when heated, and decompose at a higher temperature. If aniline is added gradually in small quantities with constant agitation to a cold concentrated solution of equal equivalents of aniline hydrochloride and ammonium vanadate, small yellow crystals separate. The solution is diluted until these crystals dissolve, and aniline is added until it no longer dissolves. The liquid is then concentrated over sulphuric acid, when the compound $2NH_2Ph,V_2O_5,2H_2O$ crystallises in large pale-yellow plates mixed with reddish-brown crystals of the preceding compound.

Aniline iodate, $NH_2Ph,2I_2O_5$, is obtained by mixing a cold almost saturated solution of ammonium iodate with an excess of aniline hydrochloride. It forms brilliant, white, nacreous plates, which alter when exposed to light, but may be kept in the dark at a low temperature. When gradually heated, it at first seems to undergo no alteration, but below a red heat it detonates very violently. If ammonium diiodate is used instead of the normal salt, decomposition of the salt begins at the moment of its formation.

Aniline chlorate is obtained in needles by mixing cold concentrated solutions of sodium chlorate and aniline hydrochloride. It is very unstable, and decomposes rapidly even in the dark at 0°. At the ordinary temperature, it quickly becomes black, and detonates violently at about 20°.

Aniline borate, $NH_2Ph,2B_2O_3,4H_2O$, analogous to ammonium biborate, is obtained by mixing the ammonium salt with aniline hydrochloride, or more easily by adding aniline to a boiling saturated solution of boric acid, in which it is readily soluble. The filtered liquid when cooled first deposits unaltered aniline, and then unctuous, transparent, white lamellæ, which lose water when heated, then intumesce and give off alkaline vapours, and finally take fire at a higher temperature.
C. H. B.

Homologues of Aniline and their Separation on a Large Scale. By O. N. WITT (*Chem. Ind.*, **10**, 8—13).—In the present communication, the author, after detailing the progress made in the manufacture of pure benzene, toluene, and xylene, since 1880, refers to the processes of separating the homologues of aniline on a commercial scale. The two nitrotoluenes are best isolated by freezing out part of the para-compound, and separating part of the ortho-derivatives by fractional distillation with steam. The medium portion is then reduced, and the toluidines thus obtained are subjected to a separation process, based on the fact that on treating a mixture of ortho- and para-toluidine with sulphuric acid insufficient in quantity to saturate both isomerides, the para-compound is first attacked. Hence on subjecting such mixtures to distillation, aided by the introduction of steam, a distillate rich in orthotoluidine is obtained. The latter may then be further purified by repeating the above treatment. The residual paratoluidine sulphate is neutralised with caustic soda or lime, and the base separated by distillation and recrystallisation. The separation of para- and meta-xylidine may be effected by sulphonating both isomerides; metaxylidinesulphonic acid is insoluble, whilst the acid from the para-compound is freely soluble, but yields an almost insoluble sodium salt, from which the base may be obtained by distillation with addition of a small amount of lime. To isolate the base from the meta-acid, the latter is heated at 160—180° under pressure with five times its weight of hydrochloric acid. The acid mixture is then saturated with soda or lime, and subjected to distillation with steam. D. B.

Butylenic Bases: Characteristics of Ethylenic Diamines. By A. Colson (*Compt. rend.*, **105**, 1014—1016).—10 grams of isobutylene bromide, boiling at 147—149°, was heated to boiling for 10 minutes with 40 c.c. of aniline, the excess of aniline expelled by distillation in a vacuum, and the aniline hydrochloride removed by treatment with water. The residue was then dissolved in warm hydrobromic acid, and the crystals which separated on cooling were purified by washing with hydrobromic acid. *Diphenylbutylenediamine hydrobromide*, $C_4H_8(C_6H_6N)_2,2HBr$, is thus obtained in white crystals, which melt at 122° with decomposition. It dissolves in five times its weight of boiling water, and 10 times its weight of cold water with partial decomposition, which is prevented if hydrobromic acid is present. It is about twice as soluble in alcohol as in water, but is not soluble in ether. The hydrobromide is decomposed completely by alkaline hydroxides with liberation of the base as a colourless oil, insoluble in water, but soluble in alcohol, ether, and chloroform. It has a bitter burning taste, and is coloured brown by nitric acid; its sp. gr. is about 1·0. With hydrochloric acid it yields a hydrochloride crystallising in white nodules, which become blue when exposed to air, melt at 98°, and dissolve in 10 times their weight of cold water with some decomposition. With acetic acid, the base forms a viscous acetate which is soluble in water, and seems to be uncrystallisable.

The aqueous solution of the base has no action on any indicator, and the alcoholic solution has no action on phthaleïns, but decolorises methyl-orange. In this respect, it resembles ethylenediphenyldiamine and ethyleneditolyldiamine, and hence it would seem that secondary aromatic diamines containing ethylene are distinguished from primary amines such as aniline and toluidine, by the fact that they are very feebly basic, and do not act on phthaleïns, but decolorise methyl-orange. The basic properties decrease as the molecular weight increases.

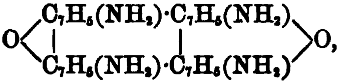
When diphenylbutylenediamine hydrobromide is treated with sodium nitrite at 0° it yields a nitroso-derivative in the form of a yellow precipitate which melts at 90°. C. H. B.

Azopseudocumene. By V. POSPĚCHOFF (*Chem. Centr.*, 1887, 858—859, from *J. Russ. Chem. Soc.*, 1887, 113—118).—Nitropseudocumene when reduced with sodium amalgam, yields *azopseudocumene*, $N_2(C_6H_3Me_3)_2$, which forms yellowish crystals melting at 173—174°, and may be sublimed without decomposition. It is sparingly soluble in alcohol, more readily in ether and benzene; it dissolves in concentrated sulphuric acid, but is reprecipitated on dilution.

The corresponding hydrazo-derivative is obtained by reducing nitropseudocumene with zinc-foil; it melts at 124—125°, and is readily oxidised in the air to the azo-derivative. In both cases, cumidine is obtained as a bye-product. V. H. V.

Formation of Aniline Dyes by the Oxidation of Aromatic Amines. By J. BARZILOFFSKY (*Chem. Centr.*, 1887, 855—857, from *J. Russ. Chem. Soc.*, 1887, 132—149).—By the oxidation of aromatic amines, azo-compounds and polyamines are formed; by changing certain conditions, basic products are formed which play an important part in the aniline dye industry. In order to throw some light on the nature of the chemical changes involved, the products of the oxidation of paratoluidine were investigated. The principal compounds formed are parazotoluene and *azotolyl*, $C_{28}H_{26}N_4$, the latter of which may also be obtained from hydroparazotoluene by heating its alcoholic solution with concentrated hydrochloric acid, as also by the oxidation of toluidine. The formation of azotolyl by the oxidation of paratoluidine is explained thus: two atoms of hydrogen are removed from two molecules of toluidine with production of hydrazotoluene, of which one part is converted into azotoluene by further oxidation, whilst the other part is transformed into the isomeric tolidine, which passes by oxidation into azotolyl.

Azotolyl when heated with an alcoholic solution of ammonium sulphite is readily transformed into the corresponding hydro-derivatiue, which differs from its analogues in readily combining with acids, and being separable on addition of alkalis. The hydrochloride, $(C_7H_7,HCl) + 1\frac{1}{2}HO$, is colourless in the pure state, but when damp is readily oxidised to a compound, *pararosotoluidine*,



$$O\left\langle\begin{array}{l} C_7H_6(NH_2)\cdot C_7H_6(NH_2) \\ \;| \qquad\qquad\qquad\; | \\ C_7H_6(NH_2)\cdot C_7H_6(NH_2) \end{array}\right\rangle O,$$

which is also obtained by oxidation of a dilute solution of paratoluidine with large excess of chromic acid, and subsequent addition of soda to the resultant product. V. H. V.

Formation of Dyes by means of Hydrogen Peroxide. By C. Wurster (*Ber.*, **20**, 2934—2940).—Ammonia is added to an emulsion of phenol and water so that a part of the phenol remains undissolved; a solution of sodium carbonate and an equal volume of hydrogen peroxide are added, and the whole diluted with water. The mixture is well shaken, a crystal of a hydroxylamine salt added, and the whole again shaken; a bright-blue and then a deep-blue coloration is produced which in a day or two changes to green. The dye which is extracted with ether is shown to be phenolquinonimide.

Hydrogen peroxide is found in the sap of many plants; it is also produced by micro-organisms, especially by the non-pathogenic.

All the monatomic phenols of the benzene series examined, in which the para-position to the hydroxyl-group is free, gave quinone-imides with hydrogen peroxide and ammonia. Hydroxy-acids also yield dyes.

Lacmoïd is formed when an ammoniacal solution of resorcinol is boiled with a little hydrogen peroxide.

If sodium carbonate is added to a mixture of resorcinol and quinone, a deep-green solution is obtained which, when shaken with air becomes yellow, then reddish-yellow and brownish-red; when air is removed, the green colour is regenerated. A similar change of colour is observed in many leaves, especially those of Berberis which contain a considerable amount of hydrogen peroxide.

Pyrocatechol, orcinol, and some plant constituents, such as phloridzin, also give dyes with hydrogen peroxide. N. H. M.

Formation of Safranines. By P. Barbier and L. Vignon (*Compt. rend.*, **105**, 939—941).—It has been shown that phenosafranine is formed by oxidising a mixture of paraphenylene diamine (1 mol.) and aniline (2 mols.), and it is known that amidoazobenzene yields paraphenylenediamine on reduction. It therefore seemed probable that the action of nitrobenzene or amidoazobenzene in presence of some reducing agent evolving hydrogen, should yield phenosafranine, and this supposition is confirmed by experiment.

Amidoazobenzene hydrochloride (1 mol.) is mixed with iron and hydrochloric acid in sufficient quantity to yield one molecular proportion (H_2) of hydrogen, and sufficient nitrobenzene to form a paste, and heated at 188° for three hours. The product is diluted with water, and treated with a current of steam to remove unchanged aniline; the aqueous solution is then mixed with ammonia, filtered, and the safranine precipitated by adding sodium chloride. The phenosafranine which separates is purified by repeated precipitation by means of salt and recrystallisation from hot water.

Amidoazotoluene likewise yields a safranine when heated with nitrobenzene, and hence it seems that this constitutes a general reaction for the preparation of safranines. C. H. B.

Nitro-derivatives of Oxanilide. By W. G. Mixter and F. O. Walther (*Amer. Chem. J.*, **9**, 355—361).—Huebner and Rudolph's work on paradinitro-oxanilide is confirmed. *Tetranitrooxanilide*, $C_2O_2[NH\cdot C_6H_3(NO_2)_2]_2$ $[NH : (NO_2)_2 = 1 : 2 : 4]$, is formed by the action of red fuming nitric acid on oxanilide; it melts at 300°, is but slightly soluble, and is easily saponified by weak potash. *Hexanitro-oxanilide*, $C_2O_2[NH{\cdot}C_6H_2(NO_2)_3]_2$ $[NH : (NO_2)_3 = 1 : 2 : 4 : 6]$, is obtained when a mixture of fuming nitric acid and strong sulphuric acid is employed; it is the highest substitution product obtainable. It melts at 300°, its best solvent is glacial acetic acid. When heated with sulphuric acid at 200°, it yields a trinitraniline melting at 188°, which is the melting point of the only known trinitraniline, $NH_2 : (NO_2)_3 = 1 : 2 : 4 : 6$. In alkaline solutions, it dissolves with formation of trinitrophenyloxanilide, trinitrophenol, and trinitraniline.

Trinitrophenyloxamide, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_6H_2(NO_2)_3$, crystallises in white fibres, and melts with decomposition at 255—260°. It has strongly marked acid characters. The potassium and ammonium salts are described. H. B.

Nitro-derivatives of Dibromoxanilide. By W. G. MIXTER and C. P. WILLCOX (*Amer. Chem. J.*, 9, 361—364).—*Dinitrodibromoxanilide*, $C_2O_2(NH{\cdot}C_6H_3Br{\cdot}NO_2)_2$ $[NH : NO_2 : Br = 1 : 2 : 4]$, is obtained by the action of strong nitric acid on paradibromoxanilide. It is yellow, melts at 288°, and when saponified yields orthonitroparabromaniline, melting at 111·4°.

Tetranitrodibromoxanilide, $C_2O_2[NH{\cdot}C_6H_2(NO_2)_2Br]_2$, is obtained with some difficulty by using red fuming nitric acid. It is white, melts at 285—287°, and does not yield dinitrobromaniline when saponified. H. B.

Compounds of Alloxan with Aromatic Amines. By G. PELLIZZARI (*Gazzetta*, 17, 409—425).—Alloxan combines directly with the aromatic amines to form additive products from which, however, the base cannot be recovered as such. Thus when a concentrated boiling aqueous solution of alloxan is agitated with α-naphthylamine, and the solution cooled, a compound of the formula $C_{14}H_{11}N_3O_4$ separates $C_4H_2N_2O_4 + C_{10}H_7NH_2 = C_{14}H_{11}N_3O_4$. This compound, *α-naphthylamine-alloxan*, crystallises in transparent, colourless needles, insoluble in water, acids, aqueous ammonia, but soluble in ether, benzene, and chloroform; it is coloured greenish by concentrated sulphuric acid. When heated with alkalis, it dissolves, yielding ammonia and the potassium salt of an acid, $C_{14}H_{10}N_2O_6$; on acidification, the acid separates in long, glistening needles, insoluble in ether, benzene, and chloroform, but very soluble in alcohol. At 110°, it loses the elements of a molecule of water, but takes it up again on recrystallisation from aqueous alcohol. β-Naphthylamine apparently does not combine with alloxan.

Aniline combines with alloxan to form *phenylamine-alloxan*,

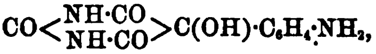
$$C_{10}H_9N_3O_4 = C_4H_2N_2O_4 + PhNH_2,$$

which crystallises in scales, decomposing at 248°. It forms a *hydrochloride*, $C_{10}H_9N_3O_4,HCl$, which crystallises in transparent needles, and a *silver* salt, $C_{10}H_8AgN_3O_4$, a white, insoluble powder. Like the naphthyl-derivative, it yields an acid, $C_9H_8N_2O_5$, when boiled with alkalis, thus: $C_{10}H_9N_3O_4 + H_2O = C_9H_8N_2O_3 + NH_3 + CO_2$. This acid crystallises in colourless needles which decompose at 180° without fusion; it is soluble in alkalis and their carbonates; its *silver* salt, $C_9H_7AgN_2O_3$, is a white crystalline precipitate. On dry distillation, phenylamine-alloxan yields *paratoluidine*.

Methylphenylamine-alloxan, $C_{11}H_{11}N_3O_4 = C_4H_2N_2O_4 + NHPhMe$, crystallises in white scales soluble in alcohol, moderately soluble in boiling water; its *hydrochloride*, $C_{11}H_{11}N_3O_4,HCl$, forms colourless prisms.

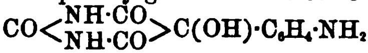
Dimethylphenylamine-alloxan, $C_{12}H_{13}N_3O_4 + H_2O$, crystallises in colourless needles, sparingly soluble in water, and decomposing at 230°. Its *hydrochloride* crystallises in transparent needles, the *nitrate* in lozenge-shaped crystals, the *oxalate* in quadrangular tables; the silver salt is a white precipitate. This compound, like the preceding, is decomposed by alkalis with formation of an acid.

To these derivatives, of which that of aniline is selected as a typical example, the author ascribes either the formula



$$CO{<}{\substack{NH\cdot CO\\ NH\cdot CO}}{>}C(OH)\cdot C_6H_4\cdot NH_2,$$

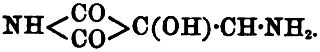
or $COOH\cdot NH\cdot CO\cdot C(CONH_2):C_6H_3\cdot NH_2$, of which the latter illustrates at once the basic and acid character, as also its decomposition by alkalis to form an acid, $C_9H_8N_2O_3$, by elimination of ammonia and carbonic anhydride, thus: $COOH\cdot NH\cdot CO(CONH_2):C_6H_3\cdot NH_2 + H_2O = COOH\cdot C(CONH_2):C_6H_3\cdot NH_2 + NH_3 + CO_2$. On the other hand, the combination of the benzene nucleus with another grouping by two of its carbon-atoms is unusual. The other formula illustrates the formation of paratoluidine by the dry distillation of the aniline compound, whilst the production of the acid compound is explained as a result of two successive reactions, in the first of which a carboxylic acid is formed which subsequently gives off a molecule of water to produce an imide, thus:



$$CO{<}{\substack{NH\cdot CO\\ NH\cdot CO}}{>}C(OH)\cdot C_6H_4\cdot NH_2 + 2H_2O =$$

$$COOH\cdot C(OH)(CONH_2)\cdot C_6H_4\cdot NH_2 + CO_2 + NH_3, \text{ and}$$

$$\text{(ii) } COOH\cdot C(OH)(CONH_2)\cdot C_6H_4\cdot NH_4 - OH_2 =$$



$$NH{<}{\substack{CO\\ CO}}{>}C(OH)\cdot CH\cdot NH_2.$$

If the latter formula be correct, then the above compounds might be considered as derivatives of dialuric acid or tartronyl carbamide.

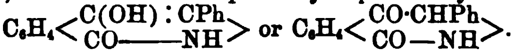
V. H. V.

Benzylidenephthalide and Isobenzalphthalide. By S. Gabriel (*Ber.*, **20**, 2863—2868).—Benzylidenephthalide crystallises in small, monoclinic forms; $a : b : c = 1\cdot9005 : 1 : 2\cdot3830$; $\beta = 76° 2\cdot5'$.

Benzylphthalimidine (Abstr., 1885, 902, 1229) is readily obtained by adding a mixture of benzalphthalimidine (12 grams) and amorphous phosphorus (6 grams) to 36 c.c. of boiling hydriodic acid (b. p. = 127°), and subsequently heating for 45 minutes in a reflux apparatus. The yield amounts to 80 per cent. of that theoretically possible. When treated with phosphorus oxychloride, and heated on a water-bath until hydrogen chloride ceases to be evolved, a product is obtained which, after extraction with water, solution in alcohol, and precipitation with ammonia, crystallises from benzene in orange- or cinnabar-red, slender needles of the composition $C_{15}H_{11}N$. This compound is soluble in chloroform, but only very sparingly in alcohol, has feeble basic properties, and forms unstable purple salts which are soluble in alcohol, and could not be analysed with the exception of the *picrate*, $C_{36}H_{25}N_5O_7$, a salt crystallising in cantharides-green prisms appearing reddish-violet by transmitted light. Phthalimidine also yields with phosphorus oxychloride a black powder having a bronze lustre; this is insoluble in all ordinary reagents and dissolves in sulphuric acid with a dark blue colour.

When isobenzalphthalide is heated with methylamine and alcohol for nine hours at 100°, it is converted into *β-desoxybenzoincarboxylmethylamide*, $COPh\cdot CH_2\cdot C_6H_4\cdot CO\cdot NMeH$; this crystallises from benzene in snow-white, matted needles, melts at 143—144°, and when heated at 200° is converted into its constituents.

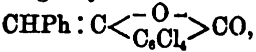
Nitrobenzylidenephthalide, on reduction with hydriodic acid and amorphous phosphorus, yields in addition to isobenzalphthalide a white powder; this crystallises from acetic acid in colourless, compact needles, begins to sinter at 240°, melts at 255—257°, and dissolves in aqueous soda or potash yielding yellow crystals of the corresponding salt. The crystals have the composition $C_{15}H_{11}NO_2$. When the compound (1 gram) is heated with methyl alcohol (10 c.c.), potassium hydroxide (1·7 gram) and methyl iodide (3 grams) at 100° for one hour, two compounds are obtained of the composition $C_{15}H_{10}NO_2Me$; one of these crystallises out on cooling in colourless, compact crystals, which begin to sinter at 200°, melt at 235—237°, and are sparingly soluble in alcohol, insoluble in alkalis, whilst the second remains in the mother-liquor and crystallises from alcohol in long, colourless needles melting at 119—121°. Since the compound is not a lactone, its constitution is probably expressed by one of the two formulæ

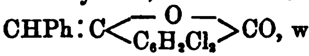


$$C_6H_4<\begin{matrix}C(OH):CPh\\CO\text{———}NH\end{matrix}> \text{ or } C_6H_4<\begin{matrix}CO\cdot CHPh\\CO-NH\end{matrix}>.$$

W. P. W.

Benzyl-derivatives. By S. GABRIEL and H. HENDESS (*Ber.*, **20**, 2869—2872).—*Metanitrobenzylphthalimide*, $NO_2\cdot C_6H_4\cdot CH_2\cdot N:C_8H_4O_2$, is formed when an intimate mixture of metanitrobenzyl chloride (1·7 gram) and potassium phthalimide (2 grams) is heated at 120° for about one hour. It crystallises in slender needles, melts at 155°, and is soluble in acetic acid and alcohol, sparingly soluble in water. When heated with fuming hydrochloric acid at 200° for two hours, it is converted into a mixture of phthalic acid and *metanitrobenzylamine hydrochloride;* the latter crystallises in needles. Metanitrobenzylamine yields an *acetyl*-derivative, $C_7H_7N_2O_2Ac$, crystallising in needles which melt at 91°, and a *platinochloride*, $(C_7H_8N_2O_2)_2,H_2PtCl_6$, crystallising in rhombic scales, whilst reduction with tin and hydrochloric acid converts it into *metamidobenzylamine;* this dissolves in water, has a strongly alkaline reaction, and forms a *picrate* crystallising in sparingly soluble scales and a *platinochloride*, $C_7H_6(NH_2)_2,H_2PtCl_6$, crystallising in yellow scales.

Benzaltetrachlorophthalide,  $CHPh\colon C{<}\genfrac{}{}{0pt}{}{-O-}{C_6Cl_4}{>}CO$, is obtained when tetrachlorophthalic anhydride (10 parts) is heated with phenylacetic acid (5 parts) and sodium acetate (½ part). It crystallises in slender, yellow needles, melts above 360°, and is practically insoluble in acetic acid and hot alcohol, more soluble in hot benzene and nitrobenzene. On treatment with sodium hydroxide, it is converted into *α-tetrachlorodesoxybenzoïnorthocarboxylic acid*, $CH_2Ph\cdot CO\cdot C_6Cl_4\cdot COOH$, which crystallises in colourless needles, melts at 175°, dissolves readily in alcohol, ether and benzene, and yields a *barium* salt, $(C_{15}H_7Cl_4O_3)_2Ba$, crystallising in pale rose-coloured needles.

Dichlorophthalic anhydride, when similarly treated, yields *benzaldichlorophthalide*,  $CHPh\colon C{<}\genfrac{}{}{0pt}{}{-O-}{C_6H_2Cl_2}{>}CO$, which crystallises in small, brownish-yellow needles, melts at 210°, dissolves readily in benzene, and by the action of alkalis is converted into *α-dichlorodesoxybenzoïnorthocarboxylic acid*, $C_{15}H_{10}Cl_2O_3$, crystallising in colourless needles melting at 117°.
W. P. W.

Resazoïn and Resorufin. By E. Ehrlich (*Monatsh.*, 8, 425—428).—Brunner and Kraemer (Abstr., 1884, 1333) proposed to drop the prefix *di-* from the names diazoresorcinol and diazoresorufin, but the author and Benedikt, contending that these compounds are no more azo- than diazo-derivatives, suggest re-naming them *resazoïn* and *resorufin*.

Resazoïn when dissolved in potash and oxidised with hydrogen peroxide yields *hydroxyresazoïn*, $C_{18}H_{12}N_2O_7$. This substance crystallises in almost colourless needles or scales which decompose before fusion, yielding a slight crystalline sublimate and leaving a carbonaceous residue. It is sparingly soluble in alcohol, soluble in glacial acetic and hydrochloric acids. Alkalis dissolve it with a reddish-yellow coloration. When reduced with zinc and sulphuric acid or ammonia, it yields a derivative of the formula $C_{18}H_{16}N_2O_7$, crystallising in needles.

These oxidation-derivatives confirm the correctness of Weselsky and Benedikt's formula $C_{18}H_{12}N_2O_6$ for resazoïn, but are not in keeping with Brunner and Kraemer's formula $C_{12}H_9NO_4$ (*loc. cit.*).
L. T. T.

Three Isomeric Tritolylstibines. By A. Michaelis and U. Genzken (*Annalen*, **242**, 164—188).—The preparation of the tritolylstibines has been previously described by the authors (Abstr., 1884, 1135). Paratritolylstibine forms hexagonal rhombohedra [$a : c = 1 : 1\cdot5807$]. Its sp. gr. at 15·6° is 1·35448 (water at 4° = 1). It melts at 127—128° and dissolves freely in chloroform. It forms additive chlorine, bromine, and iodine compounds which have already been described (*loc. cit.*). On the addition of a cold alcoholic solution of mercuric chloride to paratritolylstibine dissolved in alcohol and ether, tritolylstibinemercuric chloride is precipitated, $(C_6H_4CH_3)_3Sb,HgCl_2$, but if hot solutions are mixed, paratolylmercuric chloride, $C_6H_4Me{\cdot}HgCl$, is obtained.

Orthotritolylstibine, $Sb(C_6H_4Me)_3$, melts at 79—80°, and dissolves freely in chloroform, benzene, ether, and light petroleum. *Orthotolylmercuric chloride*, $C_6H_4Me{\cdot}HgCl$, is obtained as a crystalline powder on mixing ethereal solutions of mercuric chloride and mercury ditolyl. It melts at 145—146°. *Orthotritolylmercuric chloride* is freely soluble in chloroform and is deposited from alcohol in silky plates. Unlike the para-compound, the alcoholic solution is not decomposed on boiling, yielding tolylmercuric chloride.

In the preparation of orthotritolylstibine, needle-shaped crystals melting at 112° are obtained. The compound (probably orthoparatritolylstibine) is freely soluble in chloroform, benzene, ether, and light petroleum. With mercuric chloride, it yields a crystalline compound which melts at 164° with decomposition. The alcoholic solution is not decomposed on boiling.

Orthotritolylstibine chloride, $(C_6H_4{\cdot}CH_3)_3SbCl_2$, melts at 178—179°, the *bromide* melts at 209—210°, and the *iodide* at 174—175°. The *oxide* melts at 220° and dissolves freely in acids.

Metatritolylstibine melts at 67—68° and dissolves freely in ether, benzene, chloroform, and acetic acid. Its sp. gr. at 15·7° is 1·3957 compared with water at 4°. The additive compound with mercuric chloride melts with decomposition at 140°. The alcoholic solution is decomposed by boiling, yielding metatolylmercuric chloride, $C_6H_4Me{\cdot}HgCl$ (m. p. 159—160°). *Metatritolylstibine chloride* melts at 137—138°. It is very soluble in benzene, ether, and chloroform. The bromide has been previously described (*loc. cit.*). The *iodide* melts at 138—139° and dissolves freely in chloroform, benzene, ether, and alcohol. The *oxide* is sparingly soluble in alkalis, alcohol, benzene, chloroform, and ether. The *basic acetate*,

$$OH{\cdot}Sb(C_6H_4Me)_3{\cdot}OAc,$$

is crystalline and melts at 142—143°. *Metatritolylstibine sulphide*, $SbS(C_6H_4Me)_3$, is obtained as a crystalline compound by the action of hydrogen sulphide on a solution of tritolylstibine chloride in alcoholic ammonia. It melts at 162—163° and dissolves in chloroform and benzene. Chlorine, bromine, or iodine converts the sulphide (in solution in chloroform) into the corresponding chloride, bromide, or iodide.

W. C. W.

Decomposition of Isonitroso-compounds. By H. v. PECHMANN (*Ber.*, 20, 2904—2906; compare Abstr., 1887, 1103).—*Benzoylformaldehyde hydrate*, $COPh{\cdot}CH(OH)_2$, is obtained as follows: nitrosoacetophenone is dissolved in a strong solution of hydrogen sodium sulphite, and the double compound so obtained boiled with 10 parts of 30 per cent. sulphuric acid; on cooling, the whole solidifies to a mass of white needles, which are dissolved out in ether and recrystallised from water. It forms lustrous, colourless needles, which melt at 73° and give off water at a higher temperature. The *anhydrous aldehyde* boils at above 142° under 125 mm. pressure. The hydrate has a peculiar penetrating odour, dissolves readily in the usual solvents, reduces ammoniacal silver solution, and is converted into mandelic acid by alkalis. When the dilute aqueous solution is treated with some drops of ammonia, flakes separate which form spheres on adding acid.

Phenyltoluquinoxaline (Hinsberg, *Annalen*, **237**, 370) is formed when an aqueous aldehyde solution is warmed with toluylenediamine sulphate and sodium acetate, and crystallises in colourless needles melting at 135°. N. H. M.

Negative Nature of Organic Radicles. By V. Meyer (*Ber.*, **20**, 2944—2952).—It was shown previously that desoxybenzoïn and benzyl cyanide, when treated with sodium ethoxide and an alkyl iodide, yield derivatives in which one hydrogen-atom of the methylene-group is replaced by an alkyl radicle, whilst ethyl phenylacetate does not react under similar conditions (Abstr., 1887, 572). This reaction has now been extended to a large number of aromatic compounds containing carbonyl- and methylene-groups, and it is found that the hydrogen of the methylene-group is displaceable by an alkyl radicle only in compounds precisely analogous in constitution to desoxybenzoïn and benzyl cyanide. Under these conditions, the amides $CH_2Ph{\cdot}CO{\cdot}NEt_2$ and $CH_2Ph{\cdot}CO{\cdot}NPh_2$, the phenylpropionitrile, $CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, the nitrile of cinnamic acid, $CHPh : CH{\cdot}CN$, and methyl diphenylacetate, $CHPh_2{\cdot}COOMe$, do not yield alkyl-derivatives; aceto- and butyro-nitrile are unattacked; whilst dibenzyl ketone, $CH_2Ph{\cdot}CO{\cdot}CH_2Ph$, paraphenylenediacetonitrile, $CN{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$, and derivatives of the type $COR{\cdot}CH_2{\cdot}R'$, containing complex aromatic radicles (naphthyl, phenanthryl, &c.) readily form alkyl-compounds. The sulphone, $SO_2Ph{\cdot}CH_2Ph$, a compound which crystallises well and volatilises without decomposition, does not react with sodium ethoxide and alkyl iodides. Di- and tri-phenylmethane also do not yield alkyl-derivatives when similarly treated, whilst beautiful, violet-coloured compounds are formed by the action of sodium ethoxide on the nitro-derivatives of these hydrocarbons.

Further investigation has shown that under no condition can more than one hydrogen-atom of the methylene-group present in desoxybenzoïn be displaced by an alkyl radicle. Nor is it possible to effect a substitution of an alkyl radicle for the remaining hydrogen-atom of the methylene-group in benzoïn, $COPh{\cdot}CHPh{\cdot}OH$, or its acetyl-derivative, $COPh{\cdot}CHPh{\cdot}OAc$. Diphenylacetonitrile, $CHPh_2{\cdot}CN$, a well-characterised crystalline compound, however, is readily acted on by sodium ethoxide and haloïd alkyl-derivatives. The substitution of methyl in the phenyl-group of benzyl cyanide does not seem to interfere with the production of alkyl-derivatives, since the three isomeric methylbenzyl cyanides, $C_6H_4Me{\cdot}CH_2{\cdot}CN$, react with sodium ethoxide and benzyl chloride just as readily as benzyl cyanide itself, although the yield of the product $C_6H_4Me{\cdot}CH(C_7H_7){\cdot}CN$ is not quite the same in each case.

Like nitroethane and ethyl acetoacetate, desoxybenzoïn and benzyl cyanide combine with nitrous acid, diazobenzene, &c. The diazo-derivatives have little stability and are difficult of isolation; the isonitroso-compounds, $CO·Ph·CPh:N·OH$ and $CN·CPh:N·OH$, can readily be obtained; the latter crystallises well and is distinctly acid in character. W. P. W.

Derivatives of Dimethyl-α-Resorcylic Acid. By H. Meyer (*Monatsh.*, 8, 429—438).—*Methyl dimethyl-α-resorcylate*,

$$C_6H_3(OMe)_2·COOMe,$$

crystallises in prisms, melts at 81°, boils at 298°, and sublimes in white needles. *Methyl monomethyl-α-resorcylate*, $OH·C_6H_3(OMe)·COOMe$, which is also formed during the methylation of dimethyl-α-resorcylic acid, forms an oil boiling with partial decomposition at 315°. *Nitrodimethyl-α-resorcylic acid*, $NO_2·C_6H_2(OMe)_2·COOH$, may be formed either by heating the solid acid with nitric acid, or by adding nitric acid to an acetic acid solution of the acid. It crystallises in yellow needles or prisms, is sparingly soluble in water, easily in alcohol and glacial acetic acid, and melts at 225°, subliming at a higher temperature. It forms well-marked salts, of which those of the alkalis are easily, the others sparingly, soluble in water. On reduction, it yields *amidodimethyl-α-resorcylic acid*, $NH_2·C_6H_2(OMe)_2·COOH$, which crystallises in hexagonal plates, easily soluble in alcohol, sparingly in water, and melting with decomposition at 182°. Its *hydrochloride* and *stannochloride* crystallise in needles. The *silver* and *copper* salts are very sparingly soluble in water. The amido-acid does not yield a quinoline-derivative, and consequently the amido- (respectively nitro-) group is probably in the para-position to the carboxyl-group.

When calcium dimethyl-α-resorcylate is subjected to dry distillation, dimethylresorcinol distils over. The residue contains calcium carbonate, a resinous compound (probably an etheric-derivative of resorcinol), and the calcium salt of an acid which the author has not yet isolated. This acid melts at about 222°, gives a violet coloration with ferric chloride, and is therefore an ortho-hydroxy acid.

L. T. T.

Action of Phthalic Anhydride on Amido-acids. By L. Reese (*Annalen*, **242**, 1—22).—Drechsel has shown (Abstr., 1883, 1126) that phthalylamidoacetic acid is formed by the action of phthalic anhydride on glycocine, and he has described the properties of the acid and of several of its salts. The sodium salt is very soluble in water, but it is precipitated on the addition of alcohol to the solution. The precipitate has the composition $C_{10}H_6NO_4Na + H_2O$. The ammonium salt, $C_{10}H_6NO_4NH_4$, is prepared by adding alcoholic ammonia to an alcoholic solution of the acid; it melts at 205° with decomposition. The salt is very soluble in water; the aqueous solution loses ammonia on evaporation. When a cold solution of copper sulphate is added to the sodium salt, rhombic prisms or plates of a pale blue colour are deposited having the composition $(C_{10}H_6NO_4)_2Cu + 3H_2O$, but on mixing hot solutions the anhydrous salt is deposited in six-sided plates. When the copper salt is cautiously heated, phthalimide and benzoic acid sublime. The silver salt, $C_{10}H_6NO_4Ag$, is deposited from hot aqueous solutions in prisms. By the action of ethyl iodide on this salt, the ethylic salt, $C_{10}H_6NO_4Et$, is obtained. It crystallises in needles, dissolves freely in ether, chloroform, and hot alcohol, melts at 104—105°, and distils at a temperature above 300° without decomposition. It is quickly saponified by boiling water.

Salts of glycocinephthaloic acid are formed by neutralising hot aqueous solutions of the alkalis or alkaline earths with phthalylamidoacetic acid, and evaporating the solution. The sodium salt is amorphous. It is precipitated as a gelatinous mass on the addition of alcohol to the concentrated aqueous solution. The potassium salt is deliquescent, and crystallises in needles; the barium salt forms rhombic plates. The copper salt is deposited in needle-shaped crystals on the addition of the sodium salt to a solution of copper sulphate. The crystalline silver salt is soluble in hot water.

Phthalylamidocaproic acid, $C_{14}H_{15}NO_4$, is prepared by fusing a mixture of phthalic anhydride and leucine. The pure acid crystallises in needles, melts at 115—116°, and is soluble in alcohol and ether; on the addition of water to the alcoholic solution, the acid is deposited in the form of an oily liquid. The alcoholic solution is lævogyrate. On dry distillation, optically inactive phthalylamidocaproic acid is formed. The inactive acid can be recrystallised from hot alcohol and ether. It melts in boiling water, and the solution on cooling deposits a few crystals. The active acid forms a crystalline platodiammonium salt, $Pt(NH_3\cdot NH_3C_{14}H_{14}NO_4)_2 + 3H_2O$, insoluble in alcohol. The inactive acid forms a similar compound containing 3½ mols. H_2O, which is less soluble in cold water than the salt of the optically active acid. The copper salt is amorphous. It is soluble in alcohol, and is decomposed by heat, yielding butylphthalimide.

The phthalylamidocaproic acids are converted by the action of alkalis into leucinphthaloic acids, and finally into leucine and phthalic acid.

The sodium salt of the optically active leucinephthaloic acid is amorphous, and is deposited as a gelatinous mass on the addition of alcohol to the aqueous solution. The potassium salt, $K_2C_{14}H_{15}NO_5$, is crystalline and freely soluble in water. The barium salt is crystalline and sparingly soluble. The platodiammonium salt forms rhombic plates freely soluble in water, sparingly soluble in alcohol, and insoluble in ether. The amorphous copper salt dissolves freely in alcohol. The free acid, $COOH\cdot C_6H_4\cdot CO\cdot NH\cdot CH(COOH)\cdot CH_2Pr^{\alpha}$, is soluble in alcohol and ether. It is decomposed by boiling water, yielding phthalic acid and leucine. It melts at 130—132°, and splits up into water and phthalylamidocaproic acid (active). The potassium salt of inactive leucinephthaloic acid is deposited in crystals on the addition of alcohol to the aqueous solution. The silver salt is amorphous. The free acid melts at 152—153°, splitting up into inactive phthalylylamidocaproic acid and water. It closely resembles the optically active acid in its properties.

W. C. W.

Action of Phthalyl Dichloride on Ethyl Sodiomalonate. By J. Wislicenus (*Annalen*, **242**, 23—93).—By the action of phthalyl dichloride (1 mol.) on ethyl sodiomalonate (2 mols.) mixed with ether, a mixture of ethyl phthalylmalonate, dimalonate and phthaloxyldimalonate is obtained. The crude product is treated with water, and the ethereal solution evaporated. An oily liquid remains which deposits crystals of ethyl phthalylmalonate. In the course of a few days, ethyl phthaloxyldimalonate is also deposited. On distilling the uncrystallisable mother-liquor in a current of steam, ethyl malonate volatilises; the non-volatile oil consists of ethyl phthalyldimalonate. After it has been purified by washing with a solution of sodium carbonate, it solidifies, forming a crystalline mass.

Ethyl phthalylmalonate, $C_{15}H_{14}O_6$, is deposited from ether in triclinic prisms. The crystals are highly refractive. The ethereal salt dissolves in 14 times its weight of ether at 9°, and in 1·7 times its weight of ether at 35°. It is more soluble in alcohol. It melts at 74·5°, and on cooling the fused mass, the solidification proceeds from certain points in a peculiar and characteristic manner.

Ethyl phthaloxyldimalonate, $C_{22}H_{24}O_9$, is deposited from ether in needles and from alcohol in prisms. It requires 184 parts by weight of ether at 9°, and 174 parts of absolute alcohol at 14° for solution. It is dissolved by alkalis with an intense yellow coloration. The substance melts at 116·5° if the temperature is slowly raised, and at 106° if it is quickly heated. In the latter case, it soon solidifies and melts again at 116·5°.

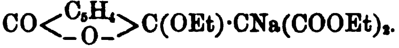
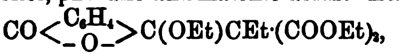
Ethyl phthalyldimalonate, $C_{22}H_{26}O_{10}$, is deposited from hot alcohol in prisms melting at 48·5°. It is freely soluble in alcohol and ether.

Ethyl phthalylmalonate is decomposed by alkalis, yielding ethyl alcohol, and phthalic and malonic acids. It also splits up on boiling with water into ethyl malonate and phthalic acid. When reduced with zinc-dust and acetic acid, it unites with four atoms of hydrogen, forming *diethyl hydrogen benzylmaloncarboxylate*,

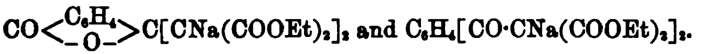
$$COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(COOEt)_2.$$

The formation of this monobasic acid is incompatible with the symmetrical formula for ethyl phthalylmalonate. The new compound is very soluble in alcohol and ether, but it requires 2230 times its weight of water at 17° for solution. It melts at 86°. The sodium salt is deliquescent and is precipitated by ether from its alcoholic solution. The silver salt, $C_{15}H_{17}AgO_6$, is soluble in hot water and is crystalline. On treatment with ethyl iodide, it yields triethyl benzylmaloncarboxylate, a colourless liquid boiling at 250° under 45 mm. pressure. *Dipotassium ethyl benzylmaloncarboxylate*, $C_8H_7(COOK)_2{\cdot}COOEt$, is formed when a solution of the potassium salt of diethylbenzylmaloncarboxylic acid is left in contact with potassium hydroxide for one hour at the ordinary temperature, but *benzylmalonorthocarboxylic acid*, $COOH{\cdot}C_6H_4{\cdot}C_2H_3(COOH)_2$, is produced if the salt is boiled with an excess of alkali and then acidified. This acid is soluble in hot water. It begins to decompose at 170°, and at 180° it is completely converted into carbonic anhydride and the hydrocinnamorthocarboxylic acid described by Gabriel and Michael (Abstr., 1878, 426).

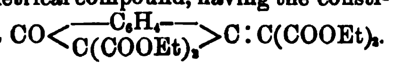
Phthalyldiamide, $C_8H_6N_2O_2$, is deposited in crystals when alcoholic ammonia is added to a solution of ethyl phthalylmalonate in absolute alcohol. It is insoluble in the usual solvents, and by boiling with water or by heating at 210° is decomposed, yielding phthalylimide.

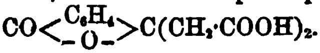
Sodium ethoxide acts on ethyl phthalylmalonate, forming *ethyl phthalyloxethylsodiomalonate*,  $CO<^{C_6H_4}_{-O-}>C(OEt)\cdot CNa(COOEt)_2$. The sodium atom is easily displaced by hydrogen, yielding ethyl phthalyloxyethylmalonate, a substance which is easily decomposed by warm alkalis, yielding ethyl alcohol, phthalic and malonic acids. *Ethyl phthalyloxyethylethylmalonate*,  $CO<^{C_6H_4}_{-O-}>C(OEt)CEt\cdot(COOEt)_2$, is formed by the action of ethyl iodide on the preceding sodium compound. It is saponified by alcoholic potash at the ordinary temperature, but the product splits up into alcohol and the potassium salt, $C_{13}H_9K_3O_7$. On the addition of hydrochloric acid to a solution of the potassium salt, benzoylorthocarboxethylmalonic acid is liberated, but it spontaneously decomposes into phthalic and malonic acids. An oily liquid which behaves in a similar manner is obtained when an acid is added to the solution of ethyl phthalylmalonate in alkalis. It is probable that the sodium compound of ethyl phthalylhydroxymalonate is formed in the first instance, and that it is converted into ethyl phthalylhydroxymalonate, which at the ordinary temperature splits up into phthalic anhydride and ethyl malonate. At 100°, ethyl monochloracetate converts the ethyl phthalyloxyethylsodiomalonate into the ethyl phthalylethylethenyltricarboxylate. On hydrolysis, this acid yields benzoylorthocarboxethenyltricarboxylic acid, which is decomposed by water, yielding ethenyltricarboxylic and phthalic acids.

Ethyl phthaloxydimalonate unites with potassium hydroxide, forming orange-coloured crystals of the composition $C_{22}H_{28}KO_{10}$. A yellow sodium compound, $C_{22}H_{24}Na_2O_{10}$, is produced by the action of an ethereal solution of ethyl phthalyldimalonate on ethyl sodiomalonate. The sodium is displaced by ethyl on treatment with ethyl iodide, and the product is decomposed by alkalis into alcohol, ethylmalonic and phthalic acids. The yellow substance is probably a mixture of the two isomerides,



$$CO<^{C_6H_4}_{-O-}>C[CNa(COOEt)_2]_2 \text{ and } C_6H_4[CO\cdot CNa(COOEt)_2]_2.$$

By the action of acetic anhydride, phthalic anhydride, or phthalic chloride on the yellow sodium compound, ethyl phthaloxyldimalonate is formed, but glacial acetic acid decomposes the substance with the formation of ethyl malonate and ethylphthalylmalonate, together with small quantities of ethyl phthalyldimalonate. Hot water also decomposes the sodium compound, yielding ethyl phthalyldimalonate (from the unsymmetrical compound), and ethyl malonate and sodium phthalate from the symmetrical isomeride. It is decomposed by bromine into ethyl phthalylmalonate and ethyl dibromomalonate, $C_{22}H_{24}Na_2O_{10} + 2Br_2 = 2NaBr + C_{15}H_{14}O_6 + CBr_2(COOEt)_2$. Ethyl phthaloxyldimalonate unites with four atoms of nascent hydrogen, forming a neutral oil of the composition $C_{22}H_{28}O_9$. Ethyl phthaloxyldimalonate is probably an unsymmetrical compound, having the constitution represented by the formula  $CO<^{C_6H_4}_{C(COOEt)_2}>C:C(COOEt)_2$.

Ethyl phthalyldimalonate dissolves in alkalis, forming an orange-coloured liquid. If the solution is heated at 100° for some hours, the colour disappears; on the addition of an acid, a tribasic acid, $COOH{\cdot}C_6H_4{\cdot}C(CH_2{\cdot}COOH)_2{\cdot}OH$, is liberated, which at once splits up into water and phthalyldiacetic acid, 
$CO<\genfrac{}{}{0pt}{}{C_6H_4}{-O-}>C(CH_2{\cdot}COOH)_2$.
A yellow potassium compound, $C_{22}H_{24}K_2O_{10} + 2H_2O$, is precipitated on the addition of ether to the orange-coloured solution of ethyl phthalyldimalonate in alcoholic potash. It is reconverted into ethyl phthalyldimalonate by the action of acids.

If phthalic chloride is added to a mixture of ether and ethyl sodiomalonate at the ordinary temperature, the chief product of the reaction is ethyl phthalylmalonate, but if half the chloride is slowly added to the warm mixture, and the product heated for some time before the remainder of the phthalic chloride is added, the chief product is ethyl phthaloxyldimalonate, a small quantity of ethyl phthalyldimalonate is also formed. By reversing the process, and adding the mixture of ether and ethyl sodium malonate to the phthalic chloride, a large yield of ethyl phthalylmalonate is obtained, together with half the weight of phthalyldimalonate, and $\frac{1}{10}$th of phthaloxyldimalonate. Phthalic anhydride acts on ethyl sodium malonate, forming sodium phthalate, ethyl phthalylmalonate and ethyl malonate.

W. C. W.

Benzenetrisulphonic Acid. By C. L. JACKSON and J. F. WING (*Amer. Chem. J.*, 9, 325—347. Compare Abstr., 1886, 623).—Senhofer prepared benzenetrisulphonic acid by heating benzene with phosphoric anhydride and fuming sulphuric acid; the authors in preparing potassium benzeneparadisulphonate also obtained benzenetrisulphonic acid; and its formation was proved to be due, during a second heating of the ingredients, to the action of potassium sulphate previously formed; a similar action possibly takes place in Claesson's method (heating a potassium sulphonate with sulphuryl chloride), and Neville and Winther's method (heating the acid sulphates of the amines). The potassium sulphate can be replaced by silver sulphate, and very imperfectly by aluminium sulphate, but not by zinc sulphate, and it therefore acts not as a dehydrating agent, but as a carrier of sulphuric acid.

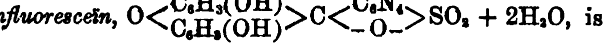
Potassium benzenetrisulphonate, $C_6H_3(SO_3K)_3 + 3H_2O$ [$= 1 : 3 : 5$], is easily prepared by heating 15 grams of potassium benzenemetadisulphonate with 18 grams of strong sulphuric acid, until the mass begins to get pasty, when it is dissolved in water and converted into the potassium salt by the usual methods; the yield amounts to 44 per cent. The preparation may be made from benzene itself, but the product is more difficult to purify owing to the formation of paradisulphonic compounds. The salt forms monoclinic plates or needles: $\beta = 68° 38\frac{1}{2}'$; $a : b = 1 : 2{\cdot}10$; 35·46 parts of the anhydrous salt are dissolved by 100 of water at 20°. Attempts to brominate or nitrate the acid were unsuccessful. *Benzenetrisulphonic chloride*, $C_6H_3(SO_2Cl)_3$, is prepared by the usual methods; it melts at 184° and soon after sublimes slowly; it is slowly decomposed by boiling water, and is best recrystallised from chloroform. *Ethyl benzenetrisulphonate*, $C_6H_3(SO_3Et)_3$, is readily obtained from the silver salt and ethyl iodide; other methods are not suitable. It melts at 147°, but is decomposed by long heating at lower temperatures. It crystallises readily from benzene, and is insoluble in water; it is decomposed by boiling with absolute alcohol, the free acid and ethyl ether being formed. *Benzenetrisulphonamide*, $C_6H_3(SO_2NH_2)_3$, is formed from the chloride by the action of aqueous ammonia. It may be crystallised from water or alcohol, and melts at 310—315°. The following salts are described, $C_6H_3(SO_2NHAg)_3$, $C_6H_3(SO_2NHHg{\cdot}OH)_3$, and $[C_6H_3(SO_2NH)_3]_2Hg$, both formed with difficulty, and $[C_6H_3(SO_3)_3]_2[Cu(NH_3)_4]_3$. Attempts to prepare the imide were not altogether successful. *Benzenetrisulphobenzoylamide*, $C_6H_3(SO_2NHBz)_3$, is obtained by acting with benzoic chloride on the sulphonamide at temperatures not above 140°. It is purified by crystallisation from alcohol, but shows no definite melting point, owing to its ready decomposition. It dissolves easily in alkalis, and forms salts such as $C_6H_3(SO_2NNaBz)_3$, and $[C_6H_3(SO_2NBz)_3]Ba_3 + 12H_2O$, both being uncrystallisable. When the benzoylamide is treated with phosphorus pentachloride, the substance

$$C_6H_3(SO_2N:CClPh)_3,$$

is formed, which by warming with aniline is converted into the compound $C_6H_3(SO_2N:CPh{\cdot}NHPh)_3$, melting at 195°, and best crystallised from alcohol. *Benzenetrisulphanilide*, $C_6H_3(SO_2NHPh)_3$, formed by the action of aniline on the sulphochloride; it crystallises well from alcohol, and melts at 237°.

The constitution of the benzenetrisulphonic acid here described is ascertained by fusion of the potassium salt with potassium cyanide and saponifying the nitrile formed, when the only product is trimesic acid; moreover, when the sulphochloride is heated with phosphorus pentachloride at 200°, it is converted into the symmetrical trichlorbenzene, hence $[(SO_3H)_3 = 1 : 3 : 5]$. H. B.

Sulphonefluoresceïn. By I. REMSEN and C. W. HAYES (*Amer. Chem. J.*, 9, 372—379).—It has been previously shown (Abstr., 1885, 539), that when resorcinol is heated with orthosulphobenzoic acid, it yields a highly fluorescent substance. This is now shown to be one of a new class of compounds, the sulphonphthaleïns.



Sulphonfluorescein, $O{<}\genfrac{}{}{0pt}{}{C_6H_3(OH)}{C_6H_3(OH)}{>}C{<}\genfrac{}{}{0pt}{}{C_6N_4}{-O-}{>}SO_2 + 2H_2O$, is obtained when orthosulphobenzoic acid is fused with resorcinol at 175—185° until the mass becomes pasty. The mass is crystallised from water, and the crystals washed with ether; they are pale straw-yellow, and probably monoclinic. It shows a feeble green fluorescence, much stronger in alkaline solution, is very soluble in water and alcohol, but dissolves only slowly in ether. It does not melt without decomposition. It has decided acid reactions, differing from fluoresceïn in that it decomposes carbonates. The barium, $(C_{19}H_{13}O_7S)_2Ba$, and calcium salts are described, as also a crystalline acetyl-derivative. When treated with bromine in acetic acid solution, it yields a dibromide, $C_{19}H_{10}Br_2O_6S$, and with sulphuric acid it yields an intensely fluorescent acid. Nascent hydrogen reduces it to a colourless substance that reoxidises in the air. H. B.

Diphthalic Acid. By C. GRAEBE and P. JUILLARD (*Annalen*, **242**, 214—257).—Pure diphthalic acid is a colourless substance which melts at 270—272°. The *methyl salt*, $C_{16}H_8O_6Me_2$, obtained by the action of methyl iodide on silver diphthalate, crystallises in plates of a lemon colour. It melts at 191—192°. The *ethyl* salt forms lemon-coloured needles, and melts at 154—155°. When hydrogen chloride is passed into warm ethyl alcohol containing diphthalic acid in solution and suspension, colourless plates are deposited of the composition $C_{18}H_{14}O_6$. The compound melts at 174°, and dissolves in alcohol, ether, and chloroform. If methyl alcohol is substituted for ethyl alcohol in the previous experiment, a crystalline compound is obtained which melts at 275°. After recrystallisation from phenol, it seems to have the composition $C_{18}H_{14}O_6$. These substances are decomposed by hydrochloric acid at 150°, yielding diphthalic acid and methyl or ethyl chloride.

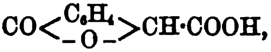
At 180°, hydroxylamine hydrochloride acts on diphthalic acid in presence of alcohol, forming a compound of the composition $C_{16}H_{18}N_2O_4$. This substance is also formed by heating at 100° in sealed tubes a mixture of hydroxylamine hydrochloride, alcohol, and diphthalic anhydride, but if the operation is carried on in an open vessel an ethereal salt is produced. The first compound crystallises in slender needles, melts at 285—286°, and dissolves in phenol.

The lactone of benzhydroltricarboxylic acid is obtained by dissolving diphthalic acid in a 4 per cent. solution of sodium hydroxide, and heating the solution at 110—115° for three minutes. When cold, the product is acidified with hydrochloric acid and the lactone is precipitated. It is soluble in choroform and in alcohol. On boiling the alcoholic solution, carbonic anhydride escapes, and the lactone of benzhydroldicarboxylic acid is formed. On reduction with phosphorus and hydriodic acid at 170°, the lactone of benzhydroltricarboxylic acid is converted into *diphenylmethanetricarboxylic acid*,

$$COOH\cdot CH(C_6H_4\cdot COOH)_2.$$

This acid is soluble in hot water and crystallises with 1 mol. H_2O. It begins to decompose at its melting point, 218—220°, and at 250—270° it is complelely converted into a red compound, $C_{16}H_8O_4$, which melts at 260°. This red substance is also formed by dissolving the acid in warm sulphuric acid and pouring the solution into water.

Benzhydroldicarboxylic acid, $OH\cdot CH(C_6H_4\cdot COOH)_2$, is formed by heating diphthalic acid with a 50 per cent. solution of potassium hydroxide at 125—130° for five minutes. The lactonic acid,



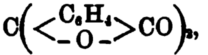
$$CO<\begin{matrix}C_6H_4\\-O-\end{matrix}>CH\cdot COOH,$$

dissolves freely in alcohol, ether, and chloroform; it melts at 203°. On oxidation, the alkaline solution yields benzophenonedicarboxylic acid, and the acid solution when treated with chromic acid yields the dilactone of the above acid. On reduction with hydriodic acid and phosphorus, diphenylmethanedicarboxylic and dihydroanthracenecarboxylic acids are obtained.

If the lactone is sublimed, the sublimate melts at 171°, and has the same composition as the lactone.

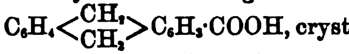
The potassium and barium salts ($C_{15}H_{10}O_5Ba + H_2O$) of benzhydroldicarboxylic acid are amorphous. The ammonium salt of the lactone is crystalline. The following salts of the lactone are insoluble in water: $(C_{15}H_9O_4)_2Ba + 2\frac{1}{2}H_2O$, $(C_{15}H_9O_4)_2Cu + 3H_2O$, and $C_{15}H_9O_4Ag$. The methyl salt melts at 154—155°, and the ethyl salt at 99·5°. The amide, $C_{15}H_9O_3{\cdot}NH_2$, crystallises in needles, and melts at 158—160°. The lactone unites with phenylhydrazine, forming the crystalline compound $C_{21}H_{16}N_2O_3$. It also forms a crystalline dinitro-derivative, $C_{15}H_8O_4(NO_2)_2$, melting between 270° and 280°. The ethyl salt, $C_{15}H_7O_4(NO_2)_2Et$, melts at 146—148°.

Benzophenonedicarboxylic acid, $CO(C_6H_4{\cdot}COOH)_2$, is soluble in alcohol, ether, and acetic acid. It melts between 150° and 155°, losing a molecule of water, and forming the dilactone. The potassium and ammonium salts crystallise in needles, and are freely soluble in water. The copper salt is insoluble, and the silver salt sparingly soluble. The *barium* salt, $C_{15}H_8O_5Ba + 5H_2O$, forms prisms, which dissolve freely in hot, and sparingly in cold water. Anthraquinone is formed when the anhydrous barium salt is strongly heated. The methyl salt, $C_{15}H_8O_5Me_2$, melts at 85—86°, and the ethyl salt at 73—74°.

The dilactone of benzophenonedicarboxylic acid,  $C\left(<{}^{C_6H_4}_{-O-}>CO\right)_2$, is obtained in crystals when strong hydrochloric acid is added to a concentrated alcoholic solution of benzophenonedicarboxylic acid. It is soluble in benzene, chloroform, hot acetic acid, and hot alcohol. When reduced with zinc-dust and acetic acid, it is converted into the lactone of benzhydroldicarboxylic acid, and when reduced with hydriodic acid and phosphorus at 170°, it yields diphenylmethanedicarboxylic acid and a small quantity of dihydroanthracenecarboxylic acid. At 200°, if much phosphorus is used, the chief product is methylanthracene hexahydride. Fuming sulphuric acid converts the dilactone into anthraquinonesulphonic acid. The imide of benzophenonedicarboxylic acid is obtained on heating the ammonium salt of the acid, or by the action of ammonia on the dilactone; it forms colourless crystals, and melts at 251—252°. It is converted into the *di-imide*, $C_{15}H_{10}O_2N_2$, by treatment with alcoholic ammonia at 140°; this is soluble in acetic acid, hot water, and hot alcohol. It crystallises in prisms, and melts at 284—286°. The acetoxime of benzophenonedicarboxylic acid forms colourless crystals, and melts at 213—214°. When the dilactone is treated with dilute alcohol and hydroxylamine hydrochloride at a gentle heat, the ethyl salt of the acetoxime is obtained; it melts at 146—149°.

Phenylhydrazine unites with benzophenonedicarboxylic acid, forming a crystalline compound of the composition $C_{21}H_{18}O_6N_2$, which melts at 155°, and loses 2 mols. H_2O, yielding the compound $C_{21}H_{14}O_4N_2$. This substance can also be prepared by slowly adding phenylhydrazine to a warm alcoholic solution of the dilactone. It melts at 230°, and is soluble in hot alcohol.

Diphenylmethanedicarboxylic acid, $CH_2(C_6H_4 \cdot COOH)_2$, melts at 254·5°, and at 280° yields a sublimate which consists of a mixture of anthraquinone and unaltered acid. The acid is soluble in alcohol and ether. It is oxidised by potassium permanganate to benzophenonedicarboxylic acid. Strong sulphuric acid at 100° converts it into α-anthranolcarboxylic acid. The barium salt, $C_{15}H_{10}O_4Ba + 6H_2O$, is crystalline. The methyl salt, $C_{15}H_{10}O_4Me_2$, is very soluble in alcohol, and melts at 43—44°.

α-Anthranolcarboxylic acid dissolves freely in alcohol and ether, and melts at 252—253°; when oxidised, it yields anthraquinonecarboxylic acid melting at 286°. *α-Dihydroanthracenecarboxylic acid*,  $C_6H_4<\substack{CH_2\\CH_2}>C_6H_3 \cdot COOH$, crystallises in yellow prisms, and is soluble in alcohol and ether. It melts at 209°, and on oxidation with potassium permanganate yields the anthraquinonecarboxlic acid which melts at 288°. *α-Methylanthracene hexahydride* crystallises in plates, and dissolves freely in alcohol, ether, and chloroform. On oxidation with a mixture of chromic and acetic acids, it yields α-methylanthraquinone, crystallising in yellow needles, and melting at 152—154°.

W. C. W.

Auramines. By W. Fehrmann (*Ber.*, **20**, 2844—2862).—Commercial auramine is the hydrochloride of a base obtained by the action of ammonium chloride on tetramethyldiamidobenzophenone; the author, however, gives to the base itself the name auramine.

Tetramethyldiamidobenzophenone (this Journ., 1876, ii, 298) crystallises in silvery-white scales, melts at 172—172·5°, and is insoluble in water, very sparingly soluble in ether, soluble in alcohol and benzene. The *hydrochloride*, $C_{17}H_{20}N_2O,2HCl$, crystallises from alcohol in small, white, radially-grouped prisms, and decomposes in aqueous solution with separation of the base; the *platinochloride*, $C_{17}H_{20}N_2O,H_2PtCl_6$, is a granular, yellow precipitate, sparingly soluble in water and alcohol; the *picrate*, $C_{17}H_{20}N_2O,C_6H_2(NO_2)_3 \cdot OH$, crystallises from alcohol in small, purple-red, radially-grouped prisms, melts at 156—157°, and is very sparingly soluble in hot water, soluble in alcohol.

Auramine hydrochloride (commercial auramine), $C_{17}H_{21}N_3,HCl + H_2O$, is prepared by heating equal parts of tetramethyldiamidobenzophenone, ammonium chloride, and zinc chloride at 150—160° until the melt is almost completely soluble in water. It crystallises from water (at 60—70°), in beautiful, yellow scales, decomposes at 265—280°, without previous fusion, and is sparingly soluble in cold water, soluble in alcohol. Dilute mineral acids readily convert it into tetramethyldiamidobenzophenone even in the cold, and the same change is effected by boiling the aqueous solution. Cotton prepared with tannin is tinged a pure yellow by the dye, and the colour is little affected by acids. *Auramine*, $NH \vdots C(C_6H_4 \cdot NMe_2)_2$, crystallises from alcohol by spontaneous evaporation in citron-yellow scales, and is insoluble in water and ether, soluble in alcohol; the *platinochloride*, $(C_{17}H_{21}N_3)_2,H_2PtCl_6$, separates from mixed aqueous solutions of the constituents as a yellow, granular precipitate, insoluble in water, and sparingly soluble in alcohol; if, however, alcoholic solutions are employed, the chief product is the platinochloride of tetramethyldiamidobenzophenone; the *picrate*,

$$C_{17}H_{21}N_3,C_6H_2(NO_2)_3 \cdot OH,$$

crystallises in slender, yellow scales, melts at 230—236°, and is insoluble in cold water, sparingly soluble in cold alcohol; the *oxalate*, $(C_{17}H_{21}N_3)_2,H_2C_2O_4$, crystallises in small, orange-yellow needles, melts at 193—194°, with the evolution of gas, and is sparingly soluble in water, soluble in warm alcohol.

Phenylauramine hydrochloride, $C_{23}H_{25}N_3,HCl$, is formed when auramine hydrochloride is heated with aniline at 175—180° until ammonia ceases to be evolved, or when tetramethyldiamidobenzophenone is heated with aniline hydrochloride. It is a reddish, crystalline mass, which dissolves in water and alcohol, and gradually in aqueous solution, or more rapidly on treatment with mineral acids, decomposes into tetramethyldiamidobenzophenone and aniline. *Phenylauramine*, $NPh \vdots C(C_6H_4 \cdot NMe_2)_2$, crystallises from alcohol in small, greyish-yellow, radially-grouped needles, decomposes at 80° into a solid and a liquid substance, and is insoluble in water and ether, soluble in alcohol; the *platinochloride*, $(C_{23}H_{25}N_3)_2,H_2PtCl_6$, and *picrate*, $C_{23}H_{25}N_3,C_5H_2(NO_2)_3 \cdot OH$, are flocculent and dissolve in alcohol.

Tolylauramine hydrochloride, obtained by heating auramine hydrochloride with paratoluidine at 160°, resembles the phenyl-derivative in its properties; the *platinochloride*, $(C_{24}H_{27}N_3)_2,H_2PtCl_6$, forms red flocks, soluble in alcohol.

Toluyleneauramine, $C_6H_3Me{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}C(C_6H_4 \cdot NMe_2)_2$, is formed when auramine hydrochloride is heated with metaparatoluylenediamine at 160°, and the resulting hydrochloride is treated with ammonia. It crystallises from alcohol in small, brown scales, and in dilute acetic acid solution dyes cotton prepared with tannin a reddish-brown. In acetic acid solution, or more rapidly on treatment with dilute mineral acids, it is decomposed into tetramethyldiamidobenzophenone. The *hydrochloride* crystallises in very slender, small, brown needles, and decomposes very readily; the *platinochloride*, $C_{24}H_{28}N_4,H_2PtCl_6$, and the *picrate*, $C_{24}H_{28}N_4,2C_6H_2(NO_2)_3OH$, are soluble in alcohol.

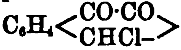
Ethyleneauramine, ${<}\begin{smallmatrix}CH_2 \cdot NH\\CH_2 \cdot NH\end{smallmatrix}{>}C(C_6H_4 \cdot NMe_2)_2$, prepared in like manner from ethylenediamine, crystallises from alcohol in yellowish scales, is insoluble in water, soluble in alcohol, and decomposes into tetramethyldiamidobenzophenone in acetic acid solution, or on treatment with mineral acids. It dyes cotton prepared with tannin yellow with a shade of red. The *hydrochloride* forms yellow needles, and is very unstable; the *platinochloride*, $C_{19}H_{26}N_4,H_2PtCl_6$, and *picrate*, $C_{19}H_{28}N_4,2C_6H_2(NO_2)_3 \cdot OH$, were also prepared.

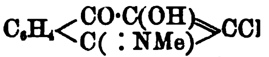
If the auramines, instead of being heated with water, are dissolved in warm alcohol, and treated with hydrogen sulphide, an analogous decomposition occurs with the production of ammonia or the corresponding amine and tetramethyldiamidothiobenzophenone. The latter crystallises in small, dark-red, flattened needles, and melts at about 164°, although by repeated crystallisation the melting point slowly rises, owing apparently to slight decomposition. When warmed with mineral acids, or when heated with water at 110—120°, it is decomposed into hydrogen sulphide and tetramethyldiamidobenzophenone. The *platinochloride*, $C_{17}H_{20}N_2S,H_2PtCl_6$ (compare Abstr., 1887, 816), forms violet-black flocks, insoluble in water and ether, sparingly soluble in alcohol, but readily soluble in excess of hydrochloric acid to a purple-red solution, which readily decomposes with the separation of platinum sulphide.

On treatment with carbon bisulphide in the cold, auramine is converted into a mixture of tetramethyldiamidothiobenzophenone and thiocyanic acid, whilst phenylauramine, when heated at 150° for five hours with carbon bisulphide, yields the thioketone and phenyl thiocarbimide. W. P. W.

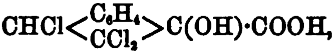
Auramine. By C. GRAEBE (*Chem. Centr.*, 1887, 951, from *Monit. Sci.*, 1887, 601).—Auramine, first obtained by Kern and Caro, is prepared by heating tetramethyldiamidobenzophenone with ammonium and zinc chlorides. The free base is colourless, the hydrochloride, which has been introduced into commerce, forms golden-yellow leaflets, sparingly soluble in cold, readily in hot water. V. H. V.

β-Naphthaquinone. By T. ZINCKE (*Ber.*, **20**, 2890—2895; compare Abstr., 1887, 53).—*Trichlorodiketohydronaphthalene hydrate*,


$C_6H_4<\begin{matrix}CO\cdot CO\\CHCl-\end{matrix}>CCl_2 + 2H_2O$, is prepared by passing chlorine into glacial acetic acid containing β-naphthaquinone, filtering, and keeping the solution for two days in a closed vessel; water is then added, and the trichloride, which separates in thin, white needles, is crystallised from alcohol or glacial acetic acid. It forms large, lustrous, well-formed crystals, probably monoclinic, which melt at 112° with separation of water; at 180°, it becomes red and gives off hydrogen chloride. The anhydrous substance forms a tough, yellowish mass, which separates from benzene in highly coloured crystals melting at 128°. When warmed with methylamine in alcoholic solution, the *compound*

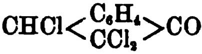

$C_6H_4<\begin{matrix}CO\cdot C(OH)\\C(:NMe)\end{matrix}>CCl$ separates in intensely red scales of a metallic lustre, melting at 200°. Two other compounds, melting at 237° and 160° respectively, are formed.

Trichlorethylenephenyleneglycollic acid,


$$CHCl<\begin{matrix}C_6H_4\\CCl_2\end{matrix}>C(OH)\cdot COOH,$$

is formed when the trichloride is dissolved in dilute aqueous soda, and separates as an oil on adding an acid. The *methyl salt* crystallises in colourless, lustrous, monoclinic crystals melting at 150°. The *acetyl-derivative* crystallises in small needles which melt at 114—116°.

Phenylenetrichlorethylene ketone,


$CHCl<\begin{matrix}C_6H_4\\CCl_2\end{matrix}>CO$, is prepared by oxidising the above hydroxy-acid with dilute chromic acid, and sepa-

rates as an oil, which gradually solidifies. It crystallises from alcohol in thick pointed needles, having a peculiar odour resembling that of benzophenone; it is readily soluble, melts at 58—59°, and distils slowly with steam.

Orthodichlorovinylbenzoic acid, $C_2HCl_2 \cdot C_6H_4 \cdot COOH$, is obtained by dissolving the trichloroketone in an alkali and adding acid. It crystallises from dilute alcohol in long, slender needles melting at 120—121°. It is reduced by sodium amalgam to orthoethylbenzoic acid melting at 68°. The *methyl salt* crystallises in thick needles which melt at 47°. N. H. M.

Hydro-derivatives of Aromatic Bases. By E. Bamberger (*Ber.*, **20**, 2915—2917).—*β-Tetrahydronaphthylamine*, $C_{10}H_{11} \cdot NH_2$, prepared by the reduction of *β*-naphthylamine with sodium, is a very strong base, capable of displacing ammonia from its salts. It forms stable, crystalline salts with carbonic anhydride, and by carbon bisulphide is converted with explosive violence into tetrahydronaphthylamine tetrahydronaphthylsulphocarbamate. The isomeric *α-derivative* is a feeble base, which does not react alkaline or yield a carbonate. It reacts like a normal amine with nitrous acid.

It is suggested that the hydro-derivatives of the aromatic bases are related to bases of the camphor-group, and that tetrahydro-*β*-naphthylamine and Leuckart and Bach's bornylamine (Abstr., 1887, 376) are similarly constituted. N. H. M.

Orthamidazo- and Hydrazimido-compounds. By T. Zincke and A. T. Lawson (*Ber.*, **20**, 2896—2903; compare Abstr., 1886, 795, and 1887, 731).—Benzeneazo-*β*-naphthylamine is a much feebler base than orthamidazotuluene; the salts are readily decomposed by alcohol and water. The *hydrochloride* crystallises in yellowish needles; the *sulphate*, $NH_2 \cdot C_{10}H_6 \cdot N_2Ph,H_2SO_4$, forms brownish-yellow needles. The *diazochloride* is prepared by dissolving 1 part of the azo-compound in 15 parts of hot glacial acetic acid and adding 3 parts of strong hydrochloric acid; cold nitrous acid is then passed through, and the whole kept until a clear, dark-red solution is obtained. The *platinochloride*, $(N_2Cl \cdot C_{10}H_6 \cdot N_2Ph)_2PtCl_4$, forms small, yellow, sparingly soluble needles. The *diazosulphate* is less soluble than the chloride; the *perbromide*, $N_2Br_3 \cdot C_{10}H_6 \cdot N_2Ph$, forms small, red needles. When the solution of the diazochloride in acetic acid is diluted with water, nitrogen is evolved, and benzeneazo-*β*-naphthol is formed. When the well-cooled acetic acid solution of the diazochloride is treated with stannous chloride, heated on a water-bath, and filtered, the *diazohydride*, $N_2H \cdot C_{10}H_6 \cdot N_2Ph$, is obtained; this crystallises from benzene or alcohol in colourless, lustrous needles, melting at 204—205°. The *acetyl-derivative*, $N_2Ac \cdot C_{10}H_6 \cdot N_2Ph$, crystallises from alcohol in lustrous needles which melt at 137—139°.

β-Amidazonaphthalene hydrochloride, $C_{10}H_7 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2,HCl$, forms small, brownish-yellow needles; the *sulphate* crystallises in brownish-yellow needles. The *diazochloride* is decomposed by water, with formation of *β*-hydroxyazonaphthalene (Nietzki and Goll, Abstr., 1886, 714) and evolution of nitrogen. The *diazohydride*, $N_2H \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_7$, crystallises in white needles melting at 202—204°, is readily soluble in hot alcohol and hot glacial acetic acid, sparingly soluble in benzene.

N. H. M.

Sulphonation of Acetonaphthalide. By M. LANGE (*Ber.*, **20**, 2940—2941).—α-Acetonaphthalide is sulphonated by adding it in fine powder to fuming sulphuric acid containing 20 per cent. of anhydride. The sulphonic acid is unstable, and loses the acetyl-group when boiled with alkalis or acids.

α-Naphthylaminesulphonic acid is obtained by treating the solution of acetonaphthalidesulphonic acid in sulphuric acid with twice the bulk of water. It crystallises in needles much more soluble than naphthionic acid; the salts are also much more soluble than those of the naphthionic acid. The solution shows a green fluorescence. The *benzylidene compound* crystallises in long needles. When the acid is diazotised and boiled with alcohol, a naphthalenesulphonic acid is formed, which yields α-naphthol when fused with potash.

N. H. M.

α-Naphthalenedisulphonic Acid. By A. WEINBERG (*Ber.*, **20**, 2906—2911).—α-Naphthalenedisulphonic acid is converted by the action of soda into a new β-naphtholsulphonic acid. This, when heated with ammonia, is converted into β-naphthylaminesulphonic acid, from which β-naphthalenemonosulphonic acid was obtained by means of the diazo-compound. Assuming that β-naphthalenedisulphonic acid has the constitution [2 : 3′], the constitution of α-naphthalenedisulphonic acid would be [2 : 2′].

ββ-Naphtholsulphonic acid, [2 : 2′] (known as naphtholsulphonic acid F.), is prepared by heating sodium naphthalenedisulphonate (100 grams), soda (30 grams), and water (300 c.c.), for 12 hours at 250°. The product is recrystallised and converted into the barium salt; the free acid is recrystallised from strong hydrochloric acid, from which it separates in needles which melt, when dried, at 89°. It is readily soluble in water and alcohol, insoluble in ether and benzene. When the sodium salt is heated with phosphorus pentachloride (3 parts) at 165°, chloronaphthol phosphate melting at 215° is formed as chief product, together with a naphthalene dichloride, which crystallises from methyl alcohol in rhombic plates which melt at 114°. *Sodium naphtholsulphonate* crystallises with 2½ mols. H_2O in large plates; the *potassium salt* with 1 mol. H_2O forms rhombic crystals. Both salts are readily soluble in water. The *magnesium salt* crystallises in plates with 5½ mols. H_2O; the *barium salt* is sparingly soluble, but more soluble than the barium salt of Schaeffer's β-naphtholsulphonic acid. Nitrous acid converts the sulphonic acid into a *nitroso-compound*; the *sodium salt* crystallises with 2 mols. H_2O in golden needles.

Naphthylaminesulphonic acid [2 : 2′] (F.), is obtained by the action of ammonia on the naphtholsulphonic acid; it dissolves in 350 parts of boiling water. The *barium salt* with 5 mols. H_2O crystallises in well-formed needles; the *magnesium salt* crystallises with 5½ mols. H_2O.

Bayer and Duisberg's β-naphthylamine-δ-sulphonic acid (Abstr., 1887, 732) is not identical with the acid [2 : 2′], but is a mixture.

β-Naphthol-δ-disulphonic acid, prepared from 2 : 2′ naphtholsulphonic acid, yields with diazobenzene a crystalline orange dye, and with α-diazonaphthalene a Bordeaux, which crystallises in violet plates. The *sodium salt* is readily soluble in water, from which it is precipitated by alcohol as a yellow powder; the *barium salt* with 2½ mols. H_2O crystallises in prisms soluble in 180 parts of boiling water. The solutions of the salts show a green fluorescence.

N. H. M.

Derivatives of Dinaphthyl. By P. JULIUS (*Chem. Ind.*, **10**, 97—99).—The author has modified Dianin's method of preparing α- and β-dinaphthol. He proposes to treat an aqueous solution of sodium naphthoxide with a mixture of ferric chloride and hydrochloric acid, whereby the naphthol, which separates in a finely-divided state, is oxidised into dinaphthol as soon as it is brought into contact with ferric chloride. The following reaction occurs :—$2C_{10}H_7{\cdot}OH + Fe_2Cl_6 = C_{20}H_{12}(OH)_2 + Fe_2Cl_4 + 2HCl$. In practice it is necessary to use 2 mols. of hydrochloric acid to 1 mol. of ferric chloride. *α-Dinaphthol* thus prepared forms a white, crystalline powder melting at 296—299°. *β-Dinaphthol* forms pale-yellow, glistening needles melting at 217°. The yields of α- and β-dinaphthols are 70 to 75 and 85 to 95 per cent. respectively as compared with theory. On treating β-dinaphthol with sulphuric acid, and saturating the resulting sulphonic acid with barium carbonate, the barium salt of *β-dinaphtholdisulphonic acid*, $C_{20}H_{10}(OH)_2(SO_3)_2Ba + 6H_2O$, separates, whilst the filtrate contains the barium salt of *β-dinaphtholtetrasulphonic acid*, $C_{20}H_8(OH)_2(SO_3)_4Ba_2$. *Dinitro-β-dinaphtholdisulphonic acid*,

$$C_{20}H_6(NO_2)_2(OH)_2(SO_3H)_2 + 3H_2O,$$

is obtained by treating the barium salt of the disulphonic acid with nitric acid. It crystallises from alcohol in yellow, silky needles. β-Dinaphthol does not combine with diazo-compounds; α-dinaphthol, however, does so readily, giving rise to a series of dyes. D. B.

Diamidopyrene. By R. JAHODA (*Monatsh.*, **8**, 449—451).—The *hydrochloride* of this base is obtained by the reduction of dinitropyrene (Goldschmiedt, Abstr., 1881, 206); it forms white needles. *Diamidopyrene*, $C_{16}H_8(NH_2)_2$, is very unstable in the free state, resinifying very rapidly. The *sulphate* forms a white substance, insoluble in water and alcohol, and decomposes when heated. L. T. T.

Diterebenthyl. By A. RENARD (*Compt. rend.*, **105**, 865—868).—The resin oils obtained by the destructive distillation of colophony consist mainly of a hydrocarbon which boils above 300°, and can be isolated by successive washings with sodium hydroxide solution, and then with water, followed by fractionation. The liquid thus obtained has the composition $C_{20}H_{30}$, and boils at 343—346°; sp. gr. at 18° = 0·9688; vapour-density 9·6; rotatory power for $[\alpha]_D = + 59°$; refractive index 1·53. It seems to be diterebenthyl, formed by the condensation of 2 molecules of terebenthene with elimination of H_2O. When exposed to air in thin layers for five days, it absorbs about one-tenth of its weight of oxygen and forms a varnish. Chromic anhydride in boiling acetic acid oxidises the hydrocarbon to carbonic oxide and carbonic anhydride. Potassium permanganate in aqueous solution converts it into carbonic anhydride and formic, acetic, and propionic acids.

When the hydrocarbon is poured gradually into well-cooled, fuming nitric acid, there is no evolution of gases, and on adding water a trinitro-derivative, $C_{20}H_{27}(NO_2)_3$, separates out. When dried in a vacuum, it forms a yellow powder soluble in alcohol and ether. If the ethereal solution of the hydrocarbon is treated with a current of hydrogen chloride, the compound $2C_{20}H_{30},HCl$ is obtained. Bromine acts violently, but in solution in carbon bisulphide it yields the dibromide $C_{20}H_{30}Br_2$, and when the carbon bisulphide evaporates, the bromine-derivative decomposes with evolution of hydrogen bromide. The direct action of bromine on the hydrocarbon in presence of water yields the hexabromo-derivative $C_{20}H_{24}Br_6$, a dark-brown, amorphous solid, which melts below 100°, and is soluble in alcohol and ether.

Ordinary concentrated sulphuric acid converts diterebenthyl into a sulphonic acid, which is isolated by agitating with water and light petroleum. The liquid separates into three layers, the lower of which is dilute sulphuric acid, the middle the sulphonic acid, and the upper layer a solution of the unaltered hydrocarbon in the light petroleum, which does not dissolve the sulphonic acid. A certain quantity of a new hydrocarbon is formed, which is not attacked by acids. The sulphonic acid is converted into the ammonium salt, which is precipitated by adding sodium chloride to the solution. The sulphonic acid, $C_{20}H_{29}\cdot SO_3H$, is obtained by decomposing the ammonium salt with sulphuric acid and extracting with benzene. It is a dark-brown mass, soluble in water, alcohol, ether, and benzene, but insoluble in light petroleum. Its solutions are highly fluorescent, and are brown by transmitted light, green by reflected light. It decomposes carbonates of the alkalis and alkaline earths. The free acid is precipitated from its aqueous solution by sodium chloride, sulphuric acid, sodium sulphate, and calcium chloride.

The ammonium salt is soluble in water, forming fluorescent solutions. The barium, calcium, copper, and lead salts, which can be obtained by double decomposition, are all insoluble in water. They all dissolve in alcohol, ether, and benzene, and burn with a smoky flame.
C. H B.

Bitter Principle of Calamus Root. By H. THOMS (*Annalen*, **242**, 257—260).—The author states that the reason Geuther (Abstr., 1887, 972) failed to obtain acorine and acoretine from calamus root is because he did not use the original process described by the author (Abstr., 1886, 895), and consequently obtained different results.
W. C. W.

Bitter Principle of Calamus Root. By A. GEUTHER (*Annalen*, **242**, 260—264).—A reply to the above.

Cubebin. By C. POMERANZ (*Monatsh.*, **8**, 466—470).—The author is investigating this compound from *Piper cubeba*, the formula of which was proved by Weidel to be $C_{10}H_{10}O_3$. Attempts to eliminate possible alkyl-groups by the action of hydrogen chloride or iodide proved unavailing, as the substance always carbonised. When oxidised with permanganate, it yielded piperonylic acid, $C_8H_6O_4$. When treated with acetic anhydride, no aceto-derivative is formed, but an ether, $(C_{10}H_{10}O_2)_2O$, which crystallises in needles, is soluble in alcohol, and melts at 78°.

From these results, the author concludes that cubebin (i) is a derivative of a methylene ether of pyrocatechol; (ii) contains a side-chain, C_3H_5O, yielding carboxyl on oxidation; and (iii) contains this side-chain in the same position relatively to the two etheric oxygen-atoms as the carboxyl in protocatechuic acid stands to the two hydroxyls.

L. T. T.

Brominated Quinolines. By A. CLAUS and V. TORNIER (*Ber.*, **20**, 2872—2882).—γ-Bromoquinoline (Claus and Collischonn, Abstr., 1887, 158) boils at 274—276° (uncorr.; not 273—274°), solidifies when cooled to below 0° and melts at 12—13°. The *oxalate* crystallises in stellate groups of prisms, melting at 107° (uncorr.). The *picrate* forms a loose, bright yellow precipitate, consisting of slender needles; it melts at 190°. The *ethobromide*, $C_9NH_6Br,EtBr$, is obtained by heating the base with ethyl bromide and absolute alcohol at 100° for some hours; it separates on cooling in lemon-coloured needles with 2 mols. EtOH, and melts at 216° (uncorr.). *γ-Bromoquinoline dibromide hydrobromide* is obtained when bromine is added to a solution of γ-bromoquinoline hydrobromide in chloroform, as a cinnabar-coloured mass of crystals, melting at 76° with decomposition; it was not analysed. When the hydrobromide is heated at about 200°, a new *dibromoquinoline* is obtained, together with its hydrobromide. The new base crystallises from alcohol in colourless, lustrous needles, which melt at 166° (uncorr.).

Parabromoquinoline is best purified by boiling with chromic acid. It is an almost colourless liquid which boils at 178° (uncorr.), solidifies when cooled to below 0°, and melts at 18—19° (uncorr.) When oxidised with potassium permanganate, it yields only quinolinic acid [$(COOH)_2 = 2 : 3$]. The *hydrobromide* forms colourless needles, which soon become red, and melt at about 256°. The hydrochloride (with 1 mol. H_2O) melts at 213° (uncorr.). The *nitrate* forms needles melting at 182°; the *sulphate* crystallises (with 1 mol. H_2O) in small plates melting when dry at 176°; the *chromate* forms small, yellow needles melting at 179°; the *oxalate*, melting at 62°, the *picrate*, melting at 216—217°, and the *ethobromide*, melting at 230° (uncorr.), are also described. *Parabromoquinoline dibromide hydrobromide* is a very unstable, orange-red substance, which melts at 70°, and when heated at 200° yields dibromoquinoline, melting at 125—126° (La Coste, *Ber.*, **14**, 925; Claus and Küttner, Abstr., 1887, 278).

Orthobromoquinoline, prepared from orthobromaniline and purified by chromic acid, forms a colourless oil boiling at 300—304° (uncorr.). The *hydrochloride*, $C_9NH_6Br,HCl + H_2O$, melts with decomposition at 166°; the *platinochloride* crystallises from alcohol in small, bright yellow needles; the *nitrate* melts at 90°; the dichromate begins to decompose at 100°, and melts at 168°.

Orthobromoquinoline dibromide hydrobromide forms orange-red crystals, melting at 90° with decomposition; when heated at 200°, a new *dibromoquinoline* is formed, which sublimes in colourless, lustrous needles melting at 90° (uncorr.).

Metabromaniline yields a mixture of two isomeric metabromoquinolines which are best separated by means of the nitrates.

Metabromoquinoline, C_9NH_6Br, is an almost colourless oil, which boils at 280° (uncorr.), and does not solidify at —4°. The *hydrochloride* (with 1 mol. H_2O) is readily soluble in water, and melts at 225° with decomposition; the *platinochloride* is a yellow, very sparingly soluble substance; the *nitrate* is readily soluble in water, and melts at 165° (uncorr.); the *dichromate* forms reddish-yellow needles, melting at 190° with previous decomposition; the *ethobromide* melts at 290° (uncorr.). *Metabromoquinoline dibromide hydrobromide* is an orange-red crystalline substance, melting at 107° (uncorr.); when heated at 200°, it yields a *dibromoquinoline* which crystallises in prisms melting at 119° (uncorr.).

Anabromoquinoline is crystalline, melts at 32° and boils at 290° (uncorr.). The *hydrochloride* (with 1 mol. H_2O) forms small branched crystals, very readily soluble in water; it melts at 213°. The *nitrate* is much more sparingly soluble in water than its isomeride, and separates in concentrically-grouped needles melting at 199° (uncorr.). The *ethobromide* crystallises from alcohol in colourless, lustrous needles melting at 214°. *Anabromoquinoline dibromide hydrobromide* forms light yellow crystals, which melt at 106—107° (uncorr.) with decomposition; when heated at 200°, *dibromoquinoline*, melting at 108° (uncorr.), is obtained. This crystallises in small, colourless needles. N. H. M.

Ethyl Hydroxyquinoline Carbonate. By E. LIPPMANN (*Monatsh.*, 8, 439—441).—When ethyl chloroformate and hydroxyquinoline are heated together, *ethyl hydroxyquinoline carbonate*, $C_9NH_6{\cdot}O{\cdot}COOEt$, is formed. This crystallises in prisms, is soluble in boiling alcohol, chloroform, and ether, melts at 105°, and gives no coloration with ferrous sulphate or ferric chloride. The *platinochloride*,

$$(C_{12}H_{11}NO_3)_2,H_2PtCl_6,$$

crystallises in orange needles.

This ethyl salt when heated with caustic soda yields alcohol, hydroxyquinoline, and sodium carbonate; with strong hydrochloric acid at 140°, it yields ethyl chloride, carbonic anhydride, and hydroxyquinoline. It is thus a carbonate and not a carboxylic acid, and is not converted into the latter even by heating at 200°. L. T. T.

Pyrenoline. By R. JAHODA (*Monatsh.*, 8, 442—448).—Amidopyrene hydrochloride (Abstr., 1881, 206) was treated by Skraup's reaction with glycerol and sulphuric acid, when *pyrenoline*, $C_{19}NH_{11}$, was formed. This substance forms yellow scales soluble in boiling alcohol, and a dilute solution shows a strong green fluorescence. It is also soluble in benzene, ether, and chloroform. It melts at 152—153°. The *hydrochloride* forms orange, microscopic needles melting at 270°; the *sulphate* pale red, hygroscopic needles melting at 246°; the *platinochloride* a red precipitate, still solid at 290°; the *methiodide* dark red, microscopic needles melting at 212°, and soluble in alcohol; and the *picrate* yellow, microscopic needles, which decompose at 260°. The latter compound is well suited for the purification of the base.

When oxidised with permanganate, an acid is formed, but has not yet been isolated. L. T. T.

Action of Sulphuric Acid on Morphine and Bibasic Acids. By P. CHASTAING and E. BARILLOT (*Compt. rend.*, **105**, 941—943, 1012—1014).—When morphine is dissolved in excess of dilute sulphuric acid, and the solution evaporated until white fumes are given off, sulphomorphide, a substance of variable composition which gives brown products with alkalis, is formed. If, however, morphine is heated with concentrated sulphuric acid at 120°, diluted with water, treated with alkalis for a very short time and then neutralised, it yields a slightly soluble compound of the composition $C_{14}H_{17}NO_4$. It always contains some sulphur in the form of sulphuryl, which is removed by strong alkalis, the compound being decomposed at the same time.

If morphine, 1 part, oxalic acid, 2 parts, and sulphuric acid, 1·5 part, are heated together at 115—120° for some hours, cooled and mixed with a large excess of water, a yellowish-white compound of the composition $C_{14}H_{17}NO_4$ or $C_{28}H_{34}N_2O_8$ is obtained. Malonic acid under similar conditions yields the compound $C_{30}H_{38}N_2O_{10}$, and succinic acid the compound $C_{32}H_{42}N_2O_{12}$. These compounds differ by $2CH_2O$. They are white, non-crystallisable substances which become greenish when exposed to air and light. They are insoluble in most neutral solvents, but are slightly soluble in cold water, more soluble in hot water. They behave like polyhydric phenols, and when mixed with alkalis oxidise on exposure to the air, forming red solutions. When these solutions are acidified, they deposit a deep blue flocculent precipitate soluble in ether, forming a violet-red solution, and in chloroform forming a blue solution, both of which deposit blue crystals of the composition $C_{26}H_{22}N_2O_4$ on evaporation.

The same compound, *morphine-blue*, is obtained with all three of the acids above-mentioned. At 100°, it contains 1 mol. H_2O, which is expelled at 120—125°. Each of the products from the bibasic acids absorbs 2 mols. of oxygen in alkaline solution, and forms 1 mol. of morphine-blue. This compound crystallises in slightly oblique prisms with a square base, which are red by transmitted light and blue by reflected light. They have no action on polarised light and melt to a blue liquid at a very high temperature. They are insoluble in water, slightly soluble in alcohol, and very soluble in ether, forming a solution which is red by transmitted light, and violet-red by reflected light. It also dissolves in chloroform, and alkalis remove the compound from both the ethereal and the chloroform solution, forming blue solutions. The compound in fact combines with alkalis to form salts which are somewhat stable when exposed to air. C. H. B.

Cinchonamine. By C. FRIEDEL (*Compt. rend.*, **105**, 985—987).—The crystals examined were obtained by Arnaud by gradually cooling an alcoholic solution. They formed hexagonal prisms terminated by rhombohedral faces, the faces of the prisms being tangent to the edges of the rhombohedron. Sometimes the latter is modified by other faces. Optical examination shows, however, that the rhombohedral form is only apparent, and the crystals really consist of three rhombic sections macled along the faces *m*, and the faces which seem to be those of the fundamental rhombohedron are really the faces a'. The fundamental form is a rhombic prism, in which $mm = 60°$, and $b : h = 1·6157$. The other angles were found to be $a'm = 47° \ 39'$; $a'p = 51° \ 4'$ (calc.), $e_1a' = 42° \ 21'$ (calc.), $e_1p = 31° \ 45'$ (calc.), $a'x = 53° \ 29'$ (calc. $53° \ 25'$) $xp = 68° \ 10'$ (calc.); $xm = 36° \ 42'$.

In two adjacent sections of the macle, $a'a' = 84° \ 42'$. There is no outward sign of the structure, the faces e_1 and *x* being perfectly united, but the macles are not always regular, especially in the larger crystals. The crystals do not become unaxial at a higher temperature

C. H. B.

Alkaloïd from Solanum Grandiflora. By D. Freire (*Compt. rend.*, **105**, 1074—1076).—The so-called "Wolf Fruit" of Brazil is the fruit of *Solanum grandiflora*, var. *pulverulentem*. Externally it is green, but the sarcocarp is white, somewhat thick, and has a bitter and disagreeable taste. It was treated with water and calcium hydroxide, evaporated to dryness on the water-bath, and the residue extracted with absolute alcohol and the solution filtered. The liquid was then concentrated to a small bulk, resinous matter being removed as it separated. After cooling, the semi-solid residue was treated with dilute hydrochloric acid, which dissolved the alkaloïd but left the resinous matter undissolved. The acid solution was decolorised by animal charcoal, precipitated with ammonia, and the precipitate washed with water and dried over sulphuric acid.

The alkaloïd thus obtained is a white substance with a very bitter taste, insoluble in water but soluble in alkalis and dilute acids. When heated with potassium hydroxide, it gives off ammonia, and its solution gives the usual reactions for alkaloïds. With platinum tetrachloride, it gives a yellow precipitate; mercuric potassium iodide, a yellow precipitate; tannin, a turbidity; ammonia, a white precipitate; concentrated sulphuric acid, an egg-yellow colour changing to red; with sulphuric acid and manganese dioxide, a yellow colour becoming first green and then violet; concentrated nitric acid, a purplish-red colour. The molecular weight as determined by means of the platinum compound is 236·4.

The author proposes to call this alkaloïd *grandiflorine*. It is an energetic poison, and the fruit itself kills sheep which eat it, hence its name.

C. H. B.

Trigonelline. By E. Jahns (*Ber.*, **20**, 2840—2843).—Trigonelline (Abstr., 1886, 85), when heated at 120° with an aqueous solution of barium hydroxide saturated at the boiling point, yields the whole of its nitrogen as methylamine, and when heated with excess of hydrochloric acid (sp. gr. = 1·2) at 260—270° is converted into nicotinic acid and a combustible gas burning with a green flame, probably methyl chloride. On these grounds, trigonelline is regarded as identical with the methylbetaïne of nicotinic acid, and a comparison of the properties of the two substances shows this to be the case.

W. P. W.

Alkaloïds extracted from the Bark of the Xanthoxylon Senegalense. By GIACOSA and MONARI (*Gazzetta*, 17, 362—367).—On extracting the bark of the *Xanthoxylon senegalense* (artar-root) with petroleum, an oil is obtained, from which a crystalline substance separates; this contains no nitrogen, and when purified has a white micaceous-appearance, melts at 120—125°, and gives a purple-red coloration with chloroform and sulphuric acid. It is probably a pseudocholesterin, but sufficient material was not at hand for a more complete investigation. The bark, after treatment with petroleum, gives on prolonged boiling with alcohol a brownish extract, from which, on addition of alkali, a yellowish solid is obtained. This consists of two alkaloïds, one of which is amorphous and insoluble in hot water, the other crystalline and soluble. The former was not further examined; the latter forms a *hydrochloride*, crystallising in minute needles or prisms, soluble in cold water, and of intensely bitter taste. The *nitrate* crystallises in needles melting at 215—220°; the *platinochloride* forms sparingly soluble yellowish prisms. The insoluble alkaloïd produces muscular irritation with coagulation of myosin, and physiological disturbances analogous to those observed with veratrine. The compounds were not analysed.

V. H. V.

Formation of Peptone. By A. CLERMONT (*Compt. rend.*, 105, 1022—1023).—20 grams of chopped meat is mixed with 30 grams of water and 0·5 gram of sulphuric acid, and heated in sealed tubes at 180° for six hours. The products are gases and a slightly brown liquid, which is easily filtered. When evaporated to dryness, ammoniacal vapours are given off, and the residue dissolves readily in water. The solution is not affected by boiling, nor by hydrochloric, nitric, or acetic acids, but it is precipitated by 4 vols. alcohol of 90°, or by tannin, mercuric chloride, or platinic chloride. 4 grams of peptone are obtained from 20 grams of fresh meat. When heated with water without any acid, the meat is converted into syntonin, which is readily converted into peptone by pepsin at 35° in a slightly acid solution.

C. H. B.

Mucin of the Submaxillary Gland. By O. HAMMARSTEN (*Zeit. physiol. Chem.* 12, 163—195).—Obolensky (*Pflüger's Archiv*, 4, 336) and Landwehr (*Zeit. physiol. Chem.*, 5, 371) have both made analyses of submaxillary mucin, but their method of preparing the mucin was faulty. In the present research, the following method was first employed: the glands were extracted with water, the extract filtered, and freed from microscopic elements by centrifugalising; acetic acid was used to precipitate the mucin from this solution; the precipitate had a stringy character. Attempts were then made to wash this precipitate free from proteïds by water acidified with acetic acid, the precipitate being repeatedly well kneaded with the acidified water; this was found to be exceedingly difficult. The mucin was redissolved in faintly alkaline water, and reprecipitated by acetic acid several times, but there was always the same difficulty in freeing it from proteïds. This was found to be due to the presence in the gland extract of a proteïd which is precipitable by acetic acid, and which is with difficulty soluble in excess of that reagent. It belongs to the class of proteïds to which the name nucleo-albumin has been given. The older method of extracting the mucin from the glands with a weak alkali was not used, because it was found that submaxillary mucin is readily decomposed by this treatment. The nucleo-albumin contains 17 per cent. of nitrogen; and it was admixture with this substance that gave in Landwehr's analyses the somewhat higher percentage of nitrogen than was found subsequently in the present research. The new method ultimately adopted for the preparation of the mucin was as follows: the clear watery extract was acidified with hydrochloric acid until the percentage of the latter reached 0·1—0·15; the mucin which was first precipitated was redissolved when the acid present reached the percentage mentioned. The mixture was then diluted with three to five times its bulk of distilled water; by this means the mucin was precipitated, and the nucleo-albumin remained in solution. This process was repeated several times, until ultimately the mucin was obtained pure. Repeated precipitation and re-solution by this method does not alter the physical properties of the precipitate, which occurs in sticky, yellowish strings, nor does it alter its chemical properties or its elementary composition. This is in contrast with what occurs with dilute alkalis; a 0·1 per cent. solution of sodium hydroxide, or saturated or half saturated lime-water dissolves the mucin; but when precipitated by acetic acid its stringy character is lost, and the precipitate is flocculent; ammonia is given off in small quantities, and the percentage of nitrogen in the precipitate increases, the precipitate probably consisting of acid albumin.

The mucin prepared in the manner described was washed with water by decantation; when free from acid, it becomes white in colour, but becomes again brownish-yellow on the addition of acetic acid; it was then washed with alcohol and ether, and dried. Elementary analysis of seven preparations gave the following average results in percentages:—C, 48·84; H, 6·8; N, 12·32; S, 0·843; ash, 0·35. Previous statements as to the absence of sulphur in mucin appear to be incorrect. The extremely small quantity of phosphorus found might have been contained in the ash. The percentage composition corresponds closely with that obtained by Loebisch (Abstr., 1886, 166), for tendon mucin. Mucin prepared in this way was found to be acid in reaction; this cannot be from union with the acid during its preparation, as the quantity of chlorine found by analysis was so excessively small; but mucin is probably itself of the nature of an acid. A neutral solution of mucin in 8 per cent. sodium chloride solution does not coagulate on heating, and even after adding acetic acid it only becomes slightly cloudy.

Alcohol precipitates mucin from a neutral solution; the precipitate is soluble in water, unless sodium chloride is present, in which case the precipitate is very insoluble. Mineral acids in small quantities precipitate mucin, and the precipitate is soluble in excess. Copper sulphate and ferric chloride, mercuric chloride, lead acetate, potassium dichromate, and potassium alum, all give slimy, gelatinous precipitates. Potassio-mercuric iodide gives no precipitate. Saturation with magnesium sulphate or sodium chloride precipitates mucin; Millon's, Adamkiewicz's, and the xanthoproteic reactions are all given by mucin. By heating with dilute mineral acids, a reducing substance is obtained. Potassium ferrocyanide gives no precipitate, or only a cloudiness in a solution of mucin in dilute hydrochloric acid. A sodium chloride solution can be pretty strongly acidified by acetic acid before precipitation occurs; and potassium ferrocyanide added to such a mixture produces no precipitate. Tannic acid in small quantities causes the liquid to become slimy and thick, and in excess causes precipitation. Of the varieties of mucin hitherto described, this approaches nearest to tendon mucin, but it differs from that in its solubility in dilute hydrochloric acid, and its behaviour to weak alkalis. W. D. H.

The Mucin of Bile. By L. PAIJKULL (*Zeit. physiol. Chem.*, **12**, 196—210).—Landwehr (*Zeit. physiol. Chem.*, **8**, 114) was the first to point out that the slimy substance in bile is not true mucin; he considered it to be a mixture of globulin with bile salts. An examination of his analytical results shows that there is some difficulty in accepting this view; for instance, the percentage of nitrogen in bile-mucin is 13·8; in paraglobulin, 15·85; and in glycocholic acid 2·5; there must therefore be 15·4 per cent. of glycocholic acid in the mixture called bile-mucin. The percentage of carbon on this calculation ought to be 55·01, but it is only 53·09. Moreover, although Landwehr states that a mixture of sodium glycocholate with serum-globulin has the physical characters of bile-mucin, it was found in this research that a mixture of globulin with bile deprived of its so-called mucin did not produce the characteristic sliminess of normal bile. The usual method of preparing mucin is not applicable to bile, as the bile-mucin is slightly soluble in excess of acetic acid. By dialysis, the mucin can be readily freed from bile salts, but not so readily from bile pigment; moreover, putrefaction is apt to ensue when dialysis is prolonged. The method ultimately adopted was to precipitate the mucin with five times its volume of absolute alcohol; the precipitate was collected and freed from alcohol by centrifugalising, redissolved in water, and again precipitated by alcohol. By thus quickly removing the alcohol, the mucin was not rendered insoluble. The properties of a 0·23 per cent. solution of this so-called mucin were as follows:—

On heating a neutral solution, it coagulated on boiling. After the addition of a trace of acetic acid, which caused no precipitation at the ordinary temperature, it coagulated on heating, like a proteïd solution. More acetic acid caused precipitation without heat, and the precipitate dissolved in excess although with some difficulty; this acetic acid solution was precipitated by potassium ferrocyanide, potassio-mercuric iodide, mercuric chloride, and tannic acid. Hydrochloric acid in very small quantities caused a flocculent precipitate, which dissolved easily in excess. Copper sulphate, ferric chloride, potassio-mercuric iodide, lead acetate, and potash alum gave abundant precipitates when added to a neutral solution. Saturation with sodium chloride or magnesium sulphate gave precipitates; the solution also gave the xanthoproteic, Millon's, and Adamkiewicz's reaction.

A solution of the mucin in hydrochloric acid (0·3 per cent.) gave no precipitate when digested for some time at 40°; but if pepsin were first added, a flocculent precipitate formed, as in solutions of nucleo-albumins. Prolonged heating with dilute mineral acids yielded no reducing substance.

The following are the results of elementary analysis:—C, 50·89; H, 6·735; N, 16·14; and S, 1·66 per cent.

The so-called mucin of bile is regarded, not as true mucin, nor as a mixture of globulin with bile salts, but as a nucleo-albumin. Small quantities of true mucin derived from the walls of the gall-bladder appear to be also present in certain cases. W. D. H.

Physiological Chemistry.

Relation of Carbohydrates in Food to Digestive Ferments. By A. Stutzer and A. Isbert (*Zeit. physiol. Chem.*, **12**, 72—94).—The question of the artificial digestion of carbohydrates is taken up from the same point of view as that of proteïds (Abstr., 1887, 361, 388, 1229); namely, can quantitative estimations be obtained of the digestible and indigestible portions of carbohydrates by the successive treatment of the fodder with the various diastatic ferments? It is already well known that certain carbohydrates, such as starch and sugar, are more digestible than certain others, such as cellulose, which is not attacked by the digestive juices, but only by putrefactive agents.

Standard solutions of ptyalin (from pig's salivary glands) of malt diastase, of pepsin, and of pancreatin were prepared; the two last being the same as those used in previous experiments. Ptyalin acts best at 40°, diastase at 60°; pancreatic fluid acts on starch better in a neutral than an alkaline fluid: not at all in an acid one. Clover-hay, wheat-meal, and white bread were the kinds of food used; and tables are given of the proteïd, fat, carbohydrate, ash, and water in each of these. Fat was in all cases first removed by extracting with ether. 2 grams of the food was used in each experiment; this was boiled with 100 c.c. of water, and when cool the ferment solution was added; 200 c.c. of the ptyalin solution with which it was kept at 37—40° for two hours: or 25 c.c. of the solution of diastase for the same length of time at 60—65°. The residue was then filtered off through asbestos, and exposed to the action of 400 c.c. of the peptic fluid; it was again freed from digestive fluids by filtration before being exposed for three hours to the action of the pancreatic ferment at 37—40°. The weight of the final residue (*minus* ash, the carbonic anhydride being driven off by nitric acid) gave the undigested organic substance (*a*); the nitrogen in this was estimated, multiplied by 6·25, and the product gives the undigested proteïd (*b*); the difference between (*a*) and (*b*) gives the undigested carbohydrate.

The *first* series of analyses are those in which the food was subjected either to the action of ptyalin or diastase, and to the subsequent action in most cases of pepsin. Full details in tabular form are given of these and the following analyses; and the following conclusions are drawn:—

(1.) A feebly alkaline solution of ptyalin acts better than a neutral, and this better again than a feebly acid one.

(2.) For substances which are rich in digestible carbohydrates, like wheat-meal, the optimum of digestion with a neutral ptyalin solution (which was the one usually employed) was obtained when 100 c.c. of the solution was present to every gram of the food. When food, such as hay, in which the digestible carbohydrates was small in quantity was used, half this amount sufficed.

(3.) 25 c.c. of the diastase solution was sufficient.

(4.) Ptyalin alone worked better than diastase, but when followed by the action of pepsin they gave identical results.

(5.) Neutral ptyalin solution dissolves some amount of proteïd.

The *second* series of analyses was one in which the pancreatic fluid alone acted. 100 c.c. of the neutral fluid gave the optimum of digestion on the carbohydrates, but the action was not so great as with ptyalin or diastase alone. Alkaline pancreatic fluid acts best on proteïds.

The *third* series were experiments in which the action of ptyalin or diastase was followed by that of the neutral pancreatic fluid: the best results being obtained when ptyalin was first used. The additional action of the pancreas is, however, very small.

The *fourth* series were experiments in which the action of either ptyalin or diastase was followed by that of both pepsin and pancreatic ferment; but the optimum was the same whether ptyalin or diastase was used. Although the pancreatic juice by itself acts on amyloïds best when neutral, yet, after the action of the other ferments, the best results are obtained when it is feebly alkaline.

It is not, however, believed that these results are comparable with what is obtained in natural digestion, because the bacteria which occur in the intestines and which act so energetically on carbohydrates, are left out of account. It is possible, however, that the method of artificial digestion may furnish us with a means of estimating cellulose quantitatively. W. D. H.

Changes in Carbohydrates in the Alimentary Canal. By J. Seegen (*Pflüger's Archiv*, **40**, 38—48).—Cane-sugar and starch are the carbohydrates most used as food; the former is inverted in the stomach (Hoppe-Seyler); the latter is converted into erythrodextrin in the stomach, and sugar is formed from it in the intestine by the action of the pancreatic and, according to some, of the intestinal juice also. Nasse named the sugar so formed ptyalose; v. Mering and

Musculus showed that this is identical with maltose. On the other hand, the sugar present in the blood and that which leaves the liver is dextrose.

The present research is devoted to a reinvestigation of these points. Animals were fed for some days on cane-sugar, and then killed; the contents of stomach and intestines were examined, and the following conclusions drawn: the stomach inverts sugar; besides cane-sugar, a certain quantity of reducing sugar was also found. The small intestine contained no cane-sugar; after boiling the contents with hydrochloric acid, the amount of sugar remained the same; the sugar present is therefore invert sugar; 24 hours after death, no sugar is found in the stomach, and only traces in the intestine, the sugar having been changed into lactic acid. In the portal blood, a certain quantity of reducing sugar is found, but after boiling with acid there was no increase in reduction, showing that cane-sugar is not absorbed as such, or if it is, in such small quantities as not to be recognisable by this method; the latter is probably the more correct statement, as cane-sugar is sometimes found in the urine.

In experiments in which starch (starch-meal, potatoes, and rice) was used, it was found that erythrodextrin was present in the stomach, but only traces of sugar which might have been formed by the saliva, The small intestine also contains dextrin, probably achroodextrin, and a reducing sugar; on boiling the contents of the small intestine with acid, the reducing power is increased; this is due to the conversion of dextrin into sugar; if the dextrin is first precipitated by alcohol, and the residue treated with acid, there is no increase in the reducing power; the sugar is therefore grape-sugar. It is possible that starch is converted into maltose by the pancreatic secretion, and then by the further action of the intestinal juice into dextrose (Brown and Heron, Abstr., 1880, 903). Absorption takes place so rapidly that only small amounts of the products of digestion are obtainable. In the portal blood, dextrose was found, and in one instance dextrin also.
W. D. H.

From what Material does the Liver form Sugar? By J. SEEGEN (*Pflüger's Archiv*, **40**, 48—64).—The liver continues to form sugar after removal from the body; in fact, as long as its cells retain vitality and the quantity formed is not in proportion to the glycogen lost (Seegen and Kratschmer, Abstr., 1882, 540). By researches of three kinds, (1) using various materials, for instance, peptones as food; (2) injecting these substances into the blood; and (3) placing the excised liver in contact with them, it was shown that peptone was one substance from which the liver forms sugar. The blood in the hepatic vein contains twice as much sugar as the portal vein, whether the food contains carbohydrate or not; fat and proteïd seem to be the substances from which the liver normally forms sugar. The sugar formed from glycogen by diastatic ferments is maltose, whereas that found in the blood leaving the liver is dextrose.

Chittenden and Lambert (*Studies from Lab. Physiol. Chem., Yale Univ.*, 1885) obtained results which showed that although the total carbohydrates are increased by peptone, the sugar is increased but little; they adhere to the view generally held that the sugar is formed from glycogen. They also speak of the sugar which leaves the liver as a mixture of maltose and dextrose. A large amount of the present paper is devoted to a criticism of the methods and results of Chittenden and Lambert. W. D. H.

Fate of Lecithin in the Body. By K. HASEBROEK (*Zeit. physiol. Chem.*, **12**, 148—162).—Bokay (*Zeit. physiol. Chem.*, **1**, 157) showed that the pancreatic juice splits lecithin into a fatty (oleic, palmitic, or stearic) acid, choline or neurine, and glycero-phosphoric acid. The question which is investigated in the present research was what happens to these three products of decomposition. The fatty acid doubtless behaves like fatty acids from adipose tissue, being partly saponified and separated from the body as calcium compounds, partly absorbed and further oxidised in the body to form carbonic anhydride and water. Choline, as has been shown by Brieger's work on ptomaïnes, is a type of poisonous alkaloïds obtained by the putrefaction of organic substances. It is perhaps here also obtained from lecithin, which has a wide distribution in the animal kingdom. Putrefaction has an important part to play in the alimentary canal. The process of putrefaction in both neurine and glycero-phosphoric acid outside the body was studied according to Hoppe-Seyler's method and with the apparatus used by him (*Zeit. physiol. Chem.*, **1**, 561). A mixture of choline hydrochloride, sewer-mud, calcium carbonate and water was kept at the ordinary temperature, and the gases which came off in large quantities were collected and analysed. They were found to consist of carbonic anhydride 18 to 20, and methane 80 to 82 per cent. After two months, when all evolution of gas had ceased, the liquid residue was examined microscopically, zoogloea colonies being found. Some was injected hypodermically in a rabbit but without ill results. On analysis it was found to contain large quantities of ammonia, and traces of first substitution products; of higher substitution basic products such as trimethylamine there was none. If a similar decomposition occurs in the intestine, it may be concluded that carbonic anhydride, methane, and ammonia are formed from choline there. This gives us a fresh source of methane in the intestine; Hoppe-Seyler and Tappenier (Abstr., 1887, 1131) have shown that cellulose is one source; and Hoppe-Seyler (Abstr., 1887, 1135) has shown that acetates form another. Choline, moreover, is not an unimportant source of marsh-gas, as lecithin is largely contained in eggs, meat, and in leguminous and other seeds.

On subjecting glycero-phosphoric acid to similar treatment, it was not found to yield any gases, or only minute quantities such as probably came from the mud used. The conclusion is therefore drawn that the acid is absorbed as such. This coincides with the observation of Sotnischewsky (*Zeit. physiol. Chem.*, **4**, 215), who found it unaltered in the urine. W. D. H.

Relative Nutritive Value of Fat and Carbohydrate. By O. KELLNER (*Zeit. physiol. Chem.*, **12**, 113—115).—By feeding a horse on starch and linseed oil respectively, and calculating the work done, it was found that the energy of one part of fat is equal to that of 2·6 parts of starch. W. D. H.

Feeding with Earth-nut and Palm Cake. By M. Schrodt (*Bied. Centr.*, 1887, 624—626).—The animals employed were cows, and they were fed with palm-nut cake containing 15 per cent. albuminoïds, whilst in the other periods of feeding they received earth-nut cake, which contained three times that quantity.

Earth-nut cake cannot be replaced by a similar quantity of palm cake without a loss of milk, fat, and dry matter,; and cotton cake produces the best results of all known cakes. E. W. P.

Change of Chemical Composition of Muscle by Fatigue. By A. Monari (*Gazzetta*, **17**, 367—385).—In this paper a further account is given of the variation of the chemical composition of muscle induced by fatigue. Full-grown dogs were killed after repose and after protracted exercise, and their muscles separated and worked up by well-known methods. The relation of creatine to creatinine was determined in each case and the results are set forth in extensive tables. The main conclusions arrived at are that (i) the proportion both of creatine and creatinine is increased by fatigue; (ii) in certain conditions of labour, the proportion of creatinine can exceed that of the creatine by one-half; (iii) in some cases the quantity of creatine in the wearied muscle is less than that present in the muscle in a state of repose, but then a greater proportion of creatine is formed owing to the transformation of the one into the other; (iv) that the creatinine is produced by transformation of the creatine; (v) xanthocreatinine is also produced, and in a proportion about one-tenth of the creatinine.
V. H. V.

Formation of Xanthocreatinine in the Organism. By A. Monari (*Gazzetta*, **17**, 360—362).—In this paper in addition to the previous observations (Abstr., 1887, 615) an analysis is given of the compound of xanthocreatinine with zinc chloride, which points to a formula $(C_5H_{10}N_4O_{21})_2,ZnCl_2$. This substance cannot however be completely separated from the similar compound with creatine. V. H. V.

Scatoxylsulphuric Acid and Scatole Pigment. By B. Mester (*Zeit. physiol. Chem.*, **12**, 130—144).—Brieger (*Zeit. physiol. Chem.*, **4**, 414) showed that scatole when administered to animals leaves the body in the urine as an ethereal hydrogen sulphate, and the chromogen of a red pigment is often also observed; this occurs also in human urine. J. Otto (*Pflüger's Archiv*, **33**, 614) obtained this pigment from the urine of a diabetic patient in considerable quantity, and showed by its reactions and analysis that it consisted of scatoxyl potassium sulphate. In the present experiments, scatole was prepared synthetically by E. Fischer's method (Abstr., 1886, 806), and it was given in doses of 6 grams daily to a dog; it was afterwards found advisable to reduce this to half, as so large a dose caused sickness occasionally but never diarrhœa. Observations were made on the relations of the normal sulphates and the ethereal hydrogen sulphates, but the variations were within normal limits. The urine passed during three weeks was collected, and G. Hoppe-Seyler's method (*Zeit. physiol. Chem.*, 7, 423) for the separation of salts of indoxylsulphuric acid was adopted for the preparation of scatoxyl potassium sulphate, but unsuccessfully, either none of the salt or the merest traces being obtained. The pigment cannot therefore be a compound of scatoxylsulphuric acid, but the chromogen is of an unknown nature. The urine used contained abundance of the pigment, which was formed by adding hydrochloric acid to an alcoholic, ethereal, or watery extract of the evaporated urine. The urine also reduced alkaline copper hydroxide solutions, and was lævorotatory. A series of observations were made on the daily relations of ordinary sulphates to ethereal hydrogen sulphates, and the quantity of pigment present in the urine during the administration of scatole. Of 12 grains given during seven days, not more than one-fifth was passed as scatoxylsulphuric acid. There is a slight increase of ethereal hydrogen sulphates produced in the urine by giving scatole, and the normal sulphates are slightly diminished. After prolonged feeding on scatole, however, the ethereal hydrogen sulphates are diminished in the urine, this may be due to scatole being an antiseptic; moreover the quantity of pigment varies without any fixed relation to the amount of these compounds. The pigment is apparently an oxidation product of the chromogen, as its formation is prevented by the simultaneous action of reducing agents like nascent hydrogen.

Elementary analyses are not concordant, but the author considers that they approach to what would be attained from scatoxyl itself; he considers that the pigment is an oxidation product of scatoxyl with a simultaneous condensation of two molecules. It is amorphous; on heating it loses 10 per cent. of water. A solution of the chromogen at first colourless becomes dark-violet and later brown on exposure to air. It dissolves in hydrochloric and sulphuric acids with a red, and in alkalis with a yellow colour. It is soluble in alcohol, amyl alcohol, ether and chloroform, but not in water. It is apparently unaltered by ammoniacal fermentation.

A certain part of the scatole is found unchanged in the fæces. The result of giving scatole as food thus differs considerably from what follows the administration of indole. The property of the urine in rotating polarised light to the left may indicate that the chromogen is a compound of glycuronic acid analogous to indoxylglycuronic acid.

This pigment is perhaps the same as the pigment described in normal human urine under various names—urorubin, urorosein, uroerythrin, purpurin, &c.

The effects of administering phenylhydrazinepyruvic acid to animals with their food shows that it is a powerful poison, producing blood in the urine among other symptoms. W. D. H.

Animal Gum. By H. A. Landwehr (*Pflüger's Archiv*, 40, 21—37).—Animal gum (Abstr., 1887, 26) is present in greater abundance in fœtal life than in extra-uterine life; it is present in the Whartonian jelly, it is in excess in the connective tissues, and the chondrogenous tissue (cartilage) which precedes the long bones appears to consist of collagen combined with animal gum; the latter compound is replaced by calcareous salts in adult bone. In some animals, as the frog, the gum is derived from the mucinoïd envelope of the eggs; in mammals, from the uterine glands, which are enormously developed during pregnancy. Pathological conditions of the female generative organs are often associated with excess of mucin or other compounds which yield gum; such as ovarian cysts, which contain metalbumin (pseudomucin): goitrous colloïd cysts do not yield gum. Myoœdema, a disease first described by Gull and Ord in women, is associated with increase of mucin in the cutaneous tissues (Charles, *Med.-Chirurg. Trans.*, **71**, 57), and may, perhaps, be associated with disease of the genital organs. Chlorosis is a form of anæmia which seems limited to women at about the age of puberty. The administration of iron in this disease causes great increase in the hæmoglobin of the blood; Hamburger, among others, has shown, however, that little or no proportion of the medicinal preparations of iron is absorbed from the alimentary canal, but iron is absorbed only in the form of organic compounds, such as are formed in the processes of plant life. Moreover, the quantity of iron is only 3 grams in the whole body, and this quantity is taken many times over during treatment. Bunge explains (Abstr., 1885, 574) the usefulness of iron in this affection by its forming iron sulphide in the intestines, removing the excess of sulphur in this way from the body; in chlorosis due to excessive fermentation processes in the alimentary canal, large quantities of hydrogen sulphide are formed, which destroy the organic compounds of iron that form hæmoglobin (hæmatogen); the administration of iron prevents this destruction of the hæmatogen. The limitation of chlorosis to the female sex, and to the time of puberty, leads the author to doubt this explanation. He regards the disease as one produced by excessive development at this period of the substances containing gum necessary for the nourishment of the embryo, and which acts injuriously on the hæmoglobin molecule; iron precipitates the gum in the alimentary canal as a jelly-like coagulum (as it does vegetable gum), and thus excess of gum leaves the body with the fæces.

The hypothesis formerly advanced as to the function of the gum in the stomach requires to be modified as follows:—In the lumen of the gastric glands which is filled with mucus, a ferment is produced by stimulation, which forms lactic acid from the gum of the mucus, and this by acting on sodium chloride produces free hydrochloric acid and sodium lactate; the former is poured into the stomach, the latter is absorbed from the glands. During digestion, the amount of sarcolactic acid in the blood is increased from 0·02 to 0·1 per cent. (Drechsel). In phosphorus poisoning, this acid is found in the urine, and also excess in the gastric juice (Cahn, Abstr., 1886, 1053); the intestinal mucus in these cases remains neutral.

In the intestine, the function of animal gum seems to be to aid the emulsion, and also the absorption of fats; pancreatic juice is not necessary for this purpose; parotid saliva, which although it contains no mucin, contains free animal gum, will emulsify fats.

Thierfelden (*Pflüger's Archiv*, **32**, 619) found that in the mammary glands milk-sugar is formed by a fermentation process, at the body temperature from a mother-substance which is not glycogen. This substance is animal gum; a watery decoction of rabbit's milk-glands was freed from proteïd by heat, from milk-sugar by two days' dialysis; it was then evaporated to a small bulk, saturated with sodium sulphate, and filtered. The filtrate contained animal gum, and gave the characteristic blue flocculi with copper hydroxide. Probably in the same way that starch is hydrated to form sugar in the intestines, and in the liver again dehydrated to form glycogen, so milk-sugar undergoes similar changes, which after being inverted into galactose in the alimentary canal is absorbed, and then dehydrated in the body, and stored as animal gum. If this is so, chlorotic people should take no carbohydrate food. In flesh feeders, it is probable that gum, like glycogen, is formed from proteïd.

Quantitative investigations on animal gum are at present impossible. The conversion of the gum, $C_6H_{10}O_5$, into gummose, $C_6H_{12}O_6$, a reducing substance, is slow and incomplete. It is, morever, precipitated at least partially by the precipitants of proteïds, neutral salts, alcohol, copper sulphate, ferric chloride, &c. W. D. H.

[*Note by Abstractor.*—Myxœdema has been since found to be present in men nearly as often as in women; no constant relation has been found to exist between disease of the generative organs and myxœdema; moreover, subsequent analyses have not confirmed Charles's statement as to the high percentage of mucin in the cutaneous tissues.]

Animal Dextran. By L. Liebermann (*Pflüger's Archiv*, **40**, 454—459).—*The Schizoneura lanuginosa* is a gall-producing louse which attacks elms. In the interior of the gall are found masses of a secretion from the animal's body which are at first clear drops, but when the galls dry up in the autumn, it consists of dirty-brown, irregular masses. The properties of this substance were investigated as follows:—The masses were finely divided, and boiled with distilled water; the resulting greenish-brown cloudy solution was decolorised to a great extent by animal charcoal, and filtered; it was acidified with hydrochloric acid, and precipitated with 96 per cent. alcohol. The precipitate was washed with alcohol, dried over sulphuric acid, and analysed; the substance contained no nitrogen, and the percentage composition corresponds very closely with the formula $C_6H_{10}O_5$. Its specific rotation is $[\alpha]_D = +156{\cdot}7$. This substance has the physical appearance of gum, is soluble with difficulty in cold, more easily in boiling water; it is insoluble in alcohol and ether, and neutral in reaction. On burning it, it gives out a smell like that of burning paper. It does not reduce copper or bismuth salts. With potash and copper sulphate, a greenish-blue, jelly-like coagulum is formed soluble in hydrochloric acid; from this acid solution, the gum is precipitated by alcohol. In the watery solution, lead acetate gives no precipitate, if alcohol is present, however, as well, it gives a precipitate; iodine gives no colour; picric acid and potash also give no reaction. On heating for a long time with dilute sulphuric acid, a substance which reduces copper oxide is formed; it differs from all known gums by its high rotatory power; it seems not to be identical with Landwehr's animal gum, and the name animal dextran (compare Scheibler, *Wagner's Jahrsber.*, 1875, 790) is suggested for it.

W. D. H.

Nephridia and Liver of Patella Vulgata. By A. B. GRIFFITHS (*Proc. Roy. Soc.*, **42**, 392—394).—The nephridia were dissected from the bodies of a large number of fresh limpets, and the secretions of the left nephridia examined separately from those of the right nephridia. Chemically, the secretions on the two sides were found to be identical; the clear liquid was first treated with hot dilute sodium hydroxide, and then hydrochloric acid added, and rhombic crystals obtained which gave the murexide test; crystals of uric acid were obtained by evaporating the secretion to dryness; the residue was taken up with absolute alcohol, filtered, dissolved in hot water; on adding excess of acetic acid to this, and allowing the mixture to stand seven hours, crystals of uric acid were obtained. The liver of patella was found to possess the functions of a true pancreas, like the "Cephalopod liver." The secretion converts starch into glucose, it produces an emulsion with fats, and a soluble ferment extracted from the cells of the gland converts fibrin into leucine and tyrosine. The secretion contains proteïds, leucine, and tyrosine, but no biliary acids. Glycogen also could not be detected in either the organ or its secretion.

W. D. H.

Absence of Uric Acid and Alkaline Reaction in the Urine of Carnivoræ. By G. SANARELLI (*Chem. Centr.*, 1887, 804—805; *from Ann. Chim. Farm.*, 1887, 273—285).—The reaction of urine from two young foxes was found to be strongly alkaline, both after a flesh and after a mixed diet; uric acid was absent and hippuric acid initially present was replaced by benzoic acid. Ammoniacal fermentation quickly set in, although the urine did not contain an abnormally large quantity of bacteria even for acid urine. Albumin, sugar and hæmatin were absent. With a flesh diet, the alkalinity increased, but with a bread diet it decreased and changed suddenly into an acid reaction, although both uric and hippuric acids were absent. The alkalinity was ascertained by means of litmus and not by phenolphthaleïn.

V. H. V.

Presence of Hydrogen Sulphide in Urine. By F. MÜLLER (*Chem. Centr.*, 1887, 807; from *Berl. klin. Wochenschr.*, **24**, 405—408 and 436—437).—The formation of hydrogen sulphide in urine from fermentation (hydrothionuria) is doubtless conditioned by micro-organisms. It is here shown that its formation is due neither to albumin nor cystin, nor potassium thiocyanate, nor yet to the presence of sulphates. On adding a solution of hydrogen sulphide to normal urine, it is quickly oxidised into water and sulphur, even in absence of air, thus showing that in cases of hydrothionuria the urine must have lost this oxidising property. On the other hand, if hydrogen sulphide is added to urine from which the hydrogen sulphide reaction originally present has disappeared, its presence could be detected for a considerable time; this proves that the bacteria consumed all the available oxygen, and thus the oxidation of the hydrogen sulphide could not ensue. V. H. V.

Ethereal Hydrogen Sulphates in Morbid Urines. By G. Hoppe-Seyler (*Zeit. physiol. Chem.*, **12**, 1—32).—Tables are given of the amounts of sulphuric acid combined as sulphates (*a*) and that combined as ethereal hydrogen sulphates; (*b*) and the ratio *a* : *b* in the urine of patients suffering from a variety of diseases. The details of the chief cases are also given. The general results obtained may, however, be summarised as follows:—Deficient or increased absorption of the normal products of digestion, as in peritonitis, tubercular diseases of the intestine, &c., leads to an increase of ethereal hydrogen sulphates in the urine, as the normal products of digestion undergo putrefactive changes, and these putrefactive products are absorbed from the intestine. In typhoid fever, there is no such increase. Simple constipation also causes no change. Diseases of the stomach in which the food lies in the stomach a long time and then undergoes fermentative changes, always lead to increase of the ethereal hydrogen sulphates. Putrefactive changes outside the alimentary canal, putrid cystitis, putrid abscesses, peritonitis putrida, &c., have the same result; and the result is proportional to the severity of the putrefaction, increased by the retention and diminished by the discharge of putrid matter as, for instance, on opening the abscess. The quantity of the ethereal hydrogen sulphates may, however, be unaltered, if at the same time other products of putrefaction are increased. Such a relation is seen between indoxyl and scatoxyl. In normal human urine, scatoxyl predominates over indoxyl; in peritonitis, the reverse the case. W. D. H.

Determination of Urea and Total Nitrogen excreted hourly in Urine. By E. Gley and C. Richet (*Compt. rend. Soc. Biol.* [8], **4**, 377—385).—Hourly determinations of the quantity of urine and the percentage of urea, extractives and total nitrogen contained therein have been made by the authors for four consecutive days. The following are the conclusions:—

1. The greatest elimination of water takes place about one hour after a meal; the greatest elimination of urea three to four hours after.
2. The excretion of water and nitrogen is much less during the night than during the day.
3. With the same diet, two persons of different body-weight excrete almost the same amount of nitrogen.
4. The ratio between the excretion of urea, extractives and total nitrogen remains almost constant throughout the 24 hours.
5. The ratio of nitrogen as urea to total nitrogen is about 4 to 5.

J. P. L.

A New Pathological Colouring Matter from Urine. By W. Leube (*Zeit. anal. Chem.*, **26**, 672).—The urine in a case of osteomalacia turned black in the air. Ether took up the colouring matter with red-violet colour, and on evaporation left it as a resinous mass, soluble for the most part in water, and wholly in ether, benzene, chloroform, and alcohol. Alkalis removed the colouring matter from its ethereal solution, becoming first brown-red and then yellow. Strong hydrochloric acid dissolved the colouring matter unchanged; the colour disappeared on heating. Zinc-dust decolorised the solution; the colour returned on exposure to air. No characteristic absorption-spectrum could be seen. M. J. S.

Urinary Pigments. By L. v. Udránszky (*Zeit. physiol. Chem.*, **12**, 33—63).—In continuation of this research (see Abstr., 1887, 1135), the first question investigated was what constituent or constituents of normal urine yield these products. Hoppe-Seyler states that humous substances, when heated with potash, yield pyrocatechuic acid, volatile fatty acids, and a non-nitrogenous acid, which are the same products as those derived from the pigment. It was found that the non-nitrogenous residue from the humous substances prepared from normal urine, from diabetic urine, or from a mixture of urea and dextrose, has the same composition. The conclusion is drawn that the dark colour which occurs in urine on treating it with mineral acids is due to a formation of such substances. They are formed by the decomposition of the reducing substance of normal urine, and their quantity stands in a constant relation to the reducing power of the urine. By boiling the urine for at least 18 hours with hydrochloric acid, the complete separation of the humous substances is brought about, and the urine loses its reducing power. The indoxyl compounds in the urine have probably only a very small influence in the formation of these substances. Humous substances containing nitrogen can be formed from carbohydrates in the presence of nascent ammonia. As Thudichum first remarked, there can no longer be any doubt that Proust's fallow resin, Scharling's omichmyl oxide, Heller's urrhodine, Schunck's indirubin, Scherer's pigment from urine, Harley's urohæmatin, and Marcet's immediate principle, are different expressions for one and the same mixture of substances, namely, of some of the products of decomposition by acids or ferments, under the influence of air or heat of the normal yellow pigment of the urine. The uropithin, uromelamin, and omicholic acid of Thudichum, Heller's urophæin, and several others can now be put into the same category; it is also possible to go a step further and say that the mother-substance of these artificially prepared pigments is the reducing substance of urine, and the normal yellow colour of urine is due to the change of carbohydrates into humous substances which has commenced inside the body.

The dark colour of the urine of herbivora (horses) depends on the presence of some constituent of the hay; the colour itself is due to a humous substance formed from this material in the fodder.

The dark colour of the urine after the administration of carbolic acid (carboluria) is also due to a similar substance. W. D. H.

Ferments in Human Fæces and in the Contents of Cysts. By R. v. Jaksch (*Zeit. physiol. Chem.*, **12**, 116—129).—The contents of abdominal cysts and ascitic fluid have a diastatic action; the blood and other tissues and fluids of the body have also been described as having a similar action. The presence of such a ferment in the contents of pancreatic cysts cannot therefore be considered diagnostic.

The fæces of children were examined for a similar ferment, and in 30 cases of various diseases, it was found that the fæces themselves, as well as a glycerol extract of them, had a marked diastatic action on starch in most cases. Sugar was tested for by Trommer's, Nylander's, Rubner's, and the phenylhydrazine tests, and abundance was found in 25 cases. In three cases only a small amount of sugar was formed; these were cases of pneumonia, rickets, and acute nephritis respectively; in two cases only (chronic intestinal catarrh and general atrophy respectively) did the ferment appear to be absent. Whether this ferment is derived from the pancreas, or is due to the action of micro-organisms, or is the result of the presence of certain proteïds (Seegen and Kratschmer having shown that egg-albumin, serum-albumin, and caseïn have an amylolytic action, *Pflüger's Archiv*, **14**, 593), is uncertain. Possibly all these factors come into account. A second series of experiments similarly conducted proved the presence of a ferment, which, with one exception, was soluble in glycerol, and which had the power of inverting cane-sugar. This ferment may be derived from the intestinal juice (O. Loew, *Pflüger's Archiv*, **27**, 203; Pavy, *Maly's Jahresber.*, **14**, 294). The action is certainly not due to the action of acids in the fæces, as it is present in alkaline fæces also.

Both these ferments are present in healthy fæces, and in adults as well as in children. Their absence in cases of disease may be found to be of diagnostic value; but this question, as well as that of the influence of these ferments on food introduced per rectum, must be left until more is known about them. The presence of ferments shows probably that some action more important than the mere absorption of water goes on in the large intestine. W. D. H.

Hæmoglobin Crystals in Septic Diseases. By C. J. BOND (*Lancet*, **2**, 1887, 509—511, 557—560).—If normal human blood is drawn from the finger, placed on a slide, and covered with a cover-glass, no crystallisation of the hæmoglobin occurs. If, however, a drop of putrid serum is added, crystallisation occurs in 24 to 48 hours. The blood drawn from the finger of patients suffering from septic poisoning has the same tendency to crystallise without the addition of any serum. In pyæmia, the effect is not so marked; in the blood from the red patches of erysipelas there is the same tendency for crystallisation to occur after removal from the body, whereas this does not occur in blood drawn from other parts of the body; in cancrum oris, which is an emphatically infective process, the same phenomenon is observed; whereas in the common zymotic diseases the blood behaves normally. The presence of sugar in the blood in diabetes, or the nitrogenous substances in uræmia, or the supposed lactic acid in rheumatism, or the bile salts in jaundice, is also not sufficient in itself to cause the crystalline tendency. In Addison's disease and in leucocythæmia, the crystalline tendency is well marked, whereas in ordinary anæmia, and often in pernicious anæmia, it is absent. In leucocythæmia the change is evidently connected with the presence of excess of white corpuscles, or some product of their decomposition; cancer cells, and the cells of other rapidly growing tumours, act similarly to leucocytes in this particular. It is found that in 10 or 12 hours after death in persons who have died from accident, the crystalline tendency is present in the blood removed from the heart, and absent in that removed from the limbs; this is probably because the blood in the heart is within easy reach of the septic gases formed in the intestines.

The larger domestic animals resemble man in the matter of crystallisation of hæmoglobin; but in the seemingly healthy mouse crystallisation occurs readily in the unaltered blood; in the cat there is a similar but not so well marked a tendency, especially in blood drawn from the splenic vein.

The occurrence of this tendency in man under the conditions described above, especially in septic diseases, is supposed to be due to the formation or presence of some ferment produced, either by the growth of bacterial organisms, or as in leucocythæmia, by the disintegration of animal cells; the stages in the change which this ferment works being first a deoxidising action on the hæmoglobin, then its exudation into the serum, and lastly crystallisation.

W. D. H.

Physiological and Therapeutical Action of Hyoscine Hydrochloride. By E. GLEY and P. RONDEAU (*Compt. rend. Soc. Biol.* [8], **4**, 56—57, and 163—164).—Hyoscine hydrochloride and hydrobromide are rapid, powerful, and unirritating mydriatics, acting more rapidly and for a more prolonged period than atropine. One drop of a 1 per cent. solution produces the maximum dilatation and paralysis of accommodation in 8 to 10 minutes.

In the rabbit and dog, the pupil of the other eye is affected, dilatation and temporary paralysis of accommodation occurring. This is not the case in man, so far as the authors' observations go.

If the cervical sympathetic of a rabbit is severed on the same side as the eye treated with the mydriatic, further dilatation of the pupil takes place on stimulating the proximal end of the nerve. The hydrochloride exercises the same effect as atropine on the inhibitory nerves of the heart, and diminishes or even suppresses the secretion of saliva, excitation of the chorda tympani with even strong currents being without effect on the submaxillary gland.

Both the hydrochloride and the hydrobromide act as powerful sedatives.

J. P. L.

Sodium Benzenesulphinate as an Antiseptic for Wounds. By E. HECKEL (*Compt. rend.*, **105**, 896—898).—This compound is readily obtained by dissolving benzoic acid in a concentrated solution of sodium sulphite. It is very soluble in water at the ordinary temperature, and has no injurious effects even in somewhat large doses. It may be applied in the form of a solution containing from 4 to 5 grams per litre. It is more efficient than phenol, and ranks with mercuric salts and iodoform, without having the poisonous properties of the former or the disagreeable smell of the latter.

C. H. B.

Naphthol as an Antiseptic Medicine. By C. BOUCHARD (*Compt. rend.*, **105**, 702—707).—β-Naphthol has already been used for external application, but has not been administered internally on account of its supposed high toxic power. From its comparative insolubility, however, it is a valuable antiseptic for deep wounds and for internal administration; 1000 c.c. of water dissolve 0·2 gram; 1000 c.c. of water containing 0·1 per cent. alcohol dissolve 0·33 gram; 1000 c.c. containing 5 per cent. alcohol dissolve 1·0 gram; 1000 c.c. containing 20 per cent. alcohol dissolve 2·0 grams. 0·33 gram of β-naphthol in 1000 c.c. of the usual cultivation liquids prevents the development of 11 species of bacteria, including those of anthrax, chicken cholera, and pneumonia, and a weak cultivation of the typhoid bacillus: it also retards the development of the bacillus of tuberculosis. It prevents the fermentation of urine, and the production of putrefaction by fæcal matter. Putrefying organic substances mixed with β-naphthol in the proportion of 0·2 gram per litre cease to putrefy, and soon lose their fœtidity.

In order to compare β-naphthol with other antiseptics, the author determined the quantity required to prevent the development of the bacillus which produces pyocyanine. 0·4 gram of β-naphthol per litre was required, and mercuric iodide was found to have six times the antiseptic power, phenol only one-sixth, creosote one-fourth. Mercuric iodide is, however, a violent poison, whilst β-naphthol may be introduced into the stomach of a rabbit in quantities not exceeding 3·8 grams per kilo. without producing death. Mercuric iodide has 250 times the toxic power. The fatal dose for a man of 65 kilos. would therefore be more than 250 grams, and it is only slightly more poisonous when injected subcutaneously. The poisonous action of β-naphthol is not observed with doses not exceeding 1·1 gram per kilo. per diem; the injurious effects previously observed must have been largely due to the mode of administration. The following table shows the comparative efficiency of the less poisonous insoluble antiseptics:—

		Doses per kilo.	
	Antiseptic.	Toxic.	Daily toxic.
Iodoform	1·27	0·50	0·05
Iodol	2·75	2·17	1·24
Naphthalene	1·51	3·40	1·00
β-Naphthol	0·40	3·80	1·10

C. H. B.

Localisation of Barium in the Organism after Chronic Poisoning with a Barium Salt. By G. LINOSSIER (*Compt. rend. Soc. Biol.* [8], **4**, 122—123).—Neumann has recently shown in the case of rabbits, that after repeated injections of the insoluble sulphate into the veins, barium is to be found in the liver, kidneys, spleen, and spinal cord, but not in the muscles, thymus, and brain.

As the insolubility of the sulphate precludes the question of chronic poisoning, the author has made a similar series of experiments with barium carbonate, prolonging the chronic poisoning for a period of 30 days. He finds on analysis that all organs contain some barium, but that it is present in very variable proportions. Lungs, muscles, and particularly the heart yield only traces, liver rather more, kidneys, brain, and spinal cord still more, and lastly bones a considerable quantity, as much as 0·56 in 1000 parts of bone ash. J. P. L.

Action of Acetanilide and Dihydroxynaphthalene on Blood. By R. LÉPINE (*Compt. rend. Soc. Biol.* [8], **4**, 517—519).—Both acetanilide and dihydroxynaphthalene when administered as drugs produce after continued use a marked anæmic condition of the patient. The number of red corpuscles rapidly diminishes, and methæmoglobin is produced. J. P. L.

Saffron Substitutes. By T. WEYL (*Ber.*, **20**, 2835—2836).—Commercial dinitrocresol is employed as a yellow colouring matter for butter, margarine, vermicelli, and confectionery. The author finds that it is poisonous, and that when introduced in aqueous solution into the stomach of rabbits in doses of 0·25 gram per kilo. it causes convulsions, paralysis of the pupil, and great difficulty in breathing, death ensuing from suffocation in from 20 to 30 minutes. Martius-yellow and the "butter-yellow" prepared by Griess from dimethylaniline and diazotised aniline are not poisonous. W. P. W.

Chemistry of Vegetable Physiology and Agriculture.

Studies on Pure Yeast. By C. AMTHOR (*Zeit. physiol. Chem.*, **12**, 64—71).—The paper consists of comparative observations on the fermentative activity on wort of eight different kinds of yeast obtained from various German breweries. Observations were made on the amount of alcohol, extractives, specific gravity, glycerol, nitrogen, and reducing substances (reckoned as maltose). The colour intensity was also observed by Stammer's colorimeter.

The wort contained 10·8 of maltose; after fermentation, the sum total of sugar (that reckoned as alcohol + the maltose in the beer) was 11·34. In reality the increase was greater, as dextrin and maltodextrin are reckoned in the above as maltose. The increase is doubtless due to the conversion of dextrin into maltose. W. D. H.

Influence of the Age of Yeast on Alcoholic Fermentation. By P. REGNARD (*Compt. rend. Soc. Biol.* [8], **4**, 442—444).—The influence on alcoholic fermentation exercised by the protoplasmic metamorphosis which occurs in the yeast cell when it is maintained under circumstances of complete starvation is represented graphically by the method introduced by the author in 1882.

The characteristic fermentation which yeast normally produces is lost after three days' complete starvation at a temperature of 25° to 30° J. P. L.

The Development of Free Nitrogen in Putrefaction and Nitrification. By O. KELLNER and T. YOSHII (*Zeit. physiol. Chem.*, **12**, 95—112).—In the first experiments, beans, milk, and fish meal were allowed to putrefy, 20 to 50 grams of each being mixed with 10 c.c. of putrid urine and 33 c.c. of water, a small quantity of gypsum being also added. The quantity of nitrogen present before and after putrefaction was practically the same; no formation of nitrates took place. In a second series of experiments with (*a*) asparagine and (*b*) beans, earth was added, and also small quantities of monocalcium phosphate, precipitated tricalcium phosphate, and magnesium sulphate, for the favourable development of organised ferments (Warington, Trans., 1884, 637); no nitrification occurred, however, even after five months, and nitrogen estimations gave the same results as in the first experiments. There is thus no loss of nitrogen during putrefaction. Dietzell in experiments similar to those of Ehrenberg (Abstr., 1887, 746) in the presence of oxygen, obtained different results. In the experiments made by the latter the putrefaction lasted six weeks, and there was no free nitrogen formed, whilst in those of the former, in which the experiments lasted 12 months, there was a loss of 15 per cent. of the nitrogen, that is to say, although putrefaction pure and simple does not cause the disengagement of gaseous nitrogen, certain processes of a secondary nature may perhaps do so. It may be due to the oxidation of ammonia by atmospheric oxygen. This could, however, not take place if organic substances are present which have a stronger affinity for oxygen; or it may be due to similar oxidation brought about by the action of nitrifying organisms, or by the action of free nitric acid on nitrogenous organic compounds; or it may be due to the reduction of nitrates and nitrites by organic substances, or, lastly, to a spontaneous decomposition of ammonium nitrate in dilute solutions.

In a third series of experiments, in which the earth used contained the nitrifying ferment, it was found that a loss of 9 to 10 per cent. of nitrogen accompanied the nitrification process; in which out of the possible ways enumerated above this takes place no definite statement can be made. Diluted sterilised solutions of ammonium nitrate do not appear to decompose spontaneously, but most probably the loss of nitrogen is due to a reaction between nitrites and organic nitrogenous compounds. When nitrification begins, the reaction of the urine, at first acid, becomes alkaline, and later neutral; this then remains unaltered. It appears possible that it is in the deeper layers of the mixture, or where the earth is specially rich in humus, that a portion of the nitrates or nitrites is reduced.

W. D. H.

Formation of Nitrogen during Putrefaction. By A. EHRENBERG (*Zeit. physiol. Chem.*, **12**, 145—147).—A few further experiments illustrating the formation of methane and carbonic anhydride in putrefaction are detailed (Abstr., 1887, 746). W. D. H.

Dependence of Assimilation of Green Cells on their Respiration of Oxygen; the part of the Plant in which Oxygen

formed in Assimilation is produced. By N. PRINGSHEIM (*Ber. Akad. Ber.*, 1887, 763—777; compare Abstr., 1886, 642).—The end cells of the leaves of *Chara fragilis* were enclosed in a microscopic gas-chamber, through which a mixture of hydrogen and carbonic anhydride (containing 1 to 5 per cent. of the latter) was passed. When light is excluded, the rotation gradually becomes less and less until at last (in 2 to 10 hours) the plasma is quite still. The cells, if not kept too long in this state, otherwise retain their original appearance, the chlorophyll apparatus remaining normal. On admitting oxygen, the rotation of the plasma again commences, unless the cells have been kept too long without oxygen after the protoplasm has ceased to rotate. If the cells are kept without oxygen just so long that the plasma still shows a slight movement, they will be found to 'have lost the power of assimilating, and when exposed to light, will no longer give off oxygen.

When the cells of *Chara* are exposed to light in a stream of hydrogen and carbonic anhydride, rotation of the plasma and evolution of oxygen cease after some time; in most cases the evolution of oxygen ceases before the rotation. The presence of the smallest amount of oxygen is sufficient (even after the rotation of the plasma has ceased for some time) to bring about movement and assimilation.

These results make it probable that in the decomposition of carbonic anhydride in plants no oxygen is formed, but that a compound is produced which decomposes at the outermost surface of the cells with evolution of oxygen.

The decomposition of carbonic anhydride and the evolution of oxygen do not occur together, but are distinct processes both as to time and place. Green and other tissues and plants in dying give off oxygen in the dark; the evolution of oxygen often continues for hours after the plant has died. N. H. M.

Assimilation and Respiration of Plants. By U. KREUSLER (*Bied. Centr.*, 1887, 669—681).—In this continuation of former experiments (*Bied. Centr.*, 1887, 110) are given the details of experiments made with shoots of the same kind of plant, *Philadelphus grandiflorus*, at different stages of growth, the temperature of observation being 15° and 25°. At a temperature of 25°, a strong and marked decrease in assimilative power accompanies increasing age of the leaf; at 15° a maximum of assimilative power is noticed in the youngest leaves. This power reaches its minimum at the period of blossom, and again rises in the oldest leaves; so that between the assimilative power in the youngest and in the oldest leaves, there does not exist much difference. A table showing the amount of water absorbed at the different temperatures is also given. In the second portion of this paper, amongst many statements concerning the absorption and exhalation of carbonic anhydride at different temperatures, it is recorded that the range of temperature in which exhalation occurs is from 0—50°, and that it is greatest at the highest temperature, the maximum appearing to be at 46·4°. Assimilation seems to take place at a lower temperature than exhalation, and it is active at 50°; but the curve representing the relation of assimilation to temperature does not agree with that representing exhalation at various temperatures. In the case of the bramble, the maximum intensity of exhalation occurs at about 46·6°, whilst that of assimilation is found at 25°. For further statements and arguments, reference must be made to the original. E. W. P.

Physiological Signification of Tannin in Vegetable Tissues. By M. WESTERMAIER (*Ber. Akad. Ber.*, 1887, 127—143).—The amount of tannin in living cells free from and containing chlorophyll increases with the amount of light to which the cells are exposed. Experiments made with *Quercus pedunculata* showed that the tannin migrates from the leaves downwards through the bark and the pith. It is uncertain whether starch and tannin migrate side by side without changing, or whether the starch migrates in the form of tannin.

In examining the leaves of *Rumex patentia* and *Rheum rhaponticum*, a substance was found which showed the starch reaction with iodine and the tannin reaction with ferric chloride and with potassium dichromate. The colour produced in the starch reaction is a bright-blue, sometimes greenish, and sometimes deep sky-blue. The substance was found in large amount in the autumn leaves of *Rheum rhaponticum*. N. H. M.

The Hop and its Constituents. By HAYDUCK (*Bied. Centr.*, 1887, 694—698).—Hops have no influence on alcoholic fermentation, but they retard, even if they do not wholly prevent, lactic fermentation, and this applies also to the butyric and other forms of like change, excepting the acetous, which is unaffected. Lerner and Bungener have shown that there exists in hops a white, crystalline compound, which they termed "hop-bitter acid." This acid, on oxidation, forms a soft resinous matter, slightly soluble in water; besides the acid, a hard resin seems to exist in large quantities, and the authors have now discovered a third, soft resin. The method whereby it may be obtained is as follows:—The hops are first exhausted with ether, and after evaporation of the ether, the residue is treated with alcohol, which leaves a white wax undissolved; solution of lead acetate is then added to the alcoholic solution, when a yellow precipitate is produced, consisting of the soft resin in combination with lead. In the filtrate from this precipitate, the two other resins are found, the one soft and soluble in light petroleum, the other hard, insoluble in light petroleum, but soluble in alcohol and ether; the former is identical with that which is an oxidation-product of hop-bitter acid. All three seem to be feeble acids, and have no definite solubility in water, but the solution of the soft resins are intensely and disagreeably bitter; whilst that of the hard resin is slightly and agreeably bitter. As regards the suppression of lactic fermentation, although the hard resin has no effect, this property belongs to the soft resins. A resinous coating sometimes forms in the wort in brewing, and it has been generally ascribed to resin, but this view is now shown to be incorrect, as this coating contains only 4·6 per cent. of resin soluble in ether, whilst nitrogenous matter was present to the extent of 13 per cent. of nitrogen. E. W. P.

Compounds extracted from Anagyris Fœtida. By N. Reali (*Gazzetta*, **17**, 325—329).—The seeds of the *Anagyris fœtida*, on extraction with ether, yield a fatty oil, two resinous substances, and also a citron-yellow compound not further examined but probably a glucoside. From an alcoholic extract, glucose, saccharose, and a yellow substance are obtained, together with a compound having all the characteristics of an alkaloïd, and called *Anagyrine*.

One of the above resinous substances which the author calls *anagyric acid* forms a lead salt, by means of which the acid can be isolated. It contains carbon, hydrogen and oxygen, but the analyses given are not very concordant. The oil is not desiccative, sp. gr. = 0·924 at 17°; on treatment with sulphuric and nitric acid, it acquires a blood-red colour. The oil yields a mixture of fatty acids on saponification. Anagyrine occurs as an amorphous mass of bitter taste, soluble in water, alcohol, ether, and benzene; it has an alkaline reaction and forms salts with acids. It gives all the reactions of alkaloïds, such as precipitates with solutions of phosphomolybdic acid, potassium bismutho-iodide, and potassium mercuro-iodide. It is unaltered at ordinary temperature by sulphuric acid, but when warmed it evolves a musk-like odour. The platinochloride is an amorphous, yellow powder, the analysis of which pointed to a formula $C_{11}H_{34}NO_8$ for anagyrine. V. H. V.

The Freezing of Ciders. By G. Lechartier (*Compt. rend.*, **105**, 723—726).—The cider was cooled at −18° to −20° until nearly completely frozen, and the liquid portion was drawn off. The mother-liquor was denser and more highly coloured than the liquid obtained by melting the ice, which in the end yielded almost pure water. The mother-liquors were kept in a cellar for some months, and at the end of that time had a very fine colour and flavour. Addition of sugar to the must merely increases the proportion of alcohol, but concentration by freezing concentrates all the soluble substances from the apples. Concentration should not be carried beyond a certain point or a disagreeable flavour is developed, and for a similar reason only ciders of good original quality are suitable for this treatment. Even when the cider is kept at −18° for 12 hours, the ferment is not killed, although fermentation is retarded. C. H. B.

Effects of an Electric Current on Wine. By F. Mengarini (*Gazzetta*, **17**, 441—450).—Blaserna and Carpéne have previously made experiments on the effects produced on wine by the action of an electric current; these have shown that various oxidation products are formed, and the wine is artificially matured. In this paper, some further experiments on this subject are described, in which a current of 3·99 ampères per hour was passed for various periods of time through a sample of Italian wine; analyses were made of the wine without and with passage of the current and the results compared. The platinum electrodes were found to be covered with albuminous substances, blackened by oxidation; there was also a considerable deposit of these substances. The proportion of alcohol was diminished partly by the slight concomitant formation of acetic acid, partly also by evaporation, and partly also by its destruction by a more profound oxidation. There was also imparted to the wine a perfume similar to that acquired by maturing; this increased by prolongation of the current. The passage of the current also assists its future preservation. The colouring matters are affected, but the author would not for the present draw any conclusions from his experiments. If by passage of an electric current the wine could be sterilised, so as to effect the complete removal of *Bacterium aceti*, this process would be of considerable technical importance. V. H. V.

Manuring Barley. By v. LIEBENBERG (*Bied. Centr.*, 1887, 649—651).—The experiments were conducted at 12 stations, and the manures employed were (1) Chili saltpetre, (2) Chili saltpetre and soluble phosphate, and (3) Chili saltpetre, soluble phosphate and potassium sulphate. The spring of the year (1886) was dry, whilst June and July were wet. There were three failures; of the remaining nine stations, the nitrogen showed itself active in producing corn and straw at seven stations, whilst an influence on the straw only was manifested at two. In two cases, potash increased the corn and straw, whilst in one it acted on the straw only; the phosphate in five cases affected the corn and straw, and in one the straw only. It seems then that nitrogen is available for barley in all localities, whilst phosphates or potash are less so. E. W. P.

Manuring Oats. By v. LIEBENBERG (*Bied. Centr.*, 1887, 651—653).—The experiments were conducted on the same principle and in the same manner as those on barley manuring. Nitrogen, and nitrogen combined with phosphate yielded an increase, but there is an uncertainty as to the gain produced by potash. Phosphates influence oats more than barley, because the former is slower and later in coming to maturity. E. W. P.

Comparative Experiments with Oats manured with Basic Slag on Moorlands. By BAESSLER (*Bied. Centr.*, 1887, 653—655).—The soil on which the experiments were conducted contained 69 per cent. organic matter, 2·7 N, 0·29 P_2O_5, and 13·66 per cent. ash. Kainite, basic slag, and superphosphates were used. Neither the super nor the slag produced any decided effects; kainite increased the yield of straw, but a general increase was remarked when the phosphates in either form were combined with kainite. The action of the slag was only 42 per cent. of that of the superphosphate, but this difference is compensated for by the lower price of the slag.
E. W. P.

Manuring Winter Wheat and Winter Rye. By v. LIEBENBERG (*Bied. Centr.*, 1887, 656—658).—The manures were the same as those employed in the author's experiments on oats and barley. No decided nor especial advantage was remarked in the crop of wheat thus manured. As regards the rye, nitrogen alone produced no effect, but when combined with phosphates or kainite there was a very decided increase. The author accounts for the absence of effect from the use of nitrogen by the fact that the land had previously received farmyard manure. E. W. P.

Manuring of Vines. By J. MORITZ and P. SEUCKER (*Bied. Centr.*, 1887, 604—609).—The experiments were instituted to determine if artificial manures could not be used for vines instead of the expensive farmyard manure. The manures were those usually employed, namely, ammonia superphosphates and potash compounds, and peat. The analyses of the must as well as its total quantity show that farmyard manure can be replaced by other manures; mineral manures seem to prevent the usual premature ripening, and consequently rotting, of some of the berries on the vines, whilst farmyard manure induces an extra growth of weeds. These experiments have been carried on for nine years, and are still being continued.

E. W. P.

Condition of Potassium in Soils, Plants, and Moulds. By BERTHELOT and ANDRÉ (*Compt. rend.*, **105**, 833—840; 911—914).—1 kilo. of the dried earth contained 23·5 grams organic carbon, 1·66 gram nitrogen at the beginning of the season and 1·73 gram. and the end, and 8·92 grams of potassium. The only methods available for the estimation of the total potassium are those in which the soil is completely decomposed by ammonium fluoride, calcium carbonate, or barium hydroxide.

Water percolating through the soil removed only 0·0029 gram of potassium per kilo., but if the soil was treated with successive quantities of water the amount dissolved increased to 0·143 gram per kilo. Heating the soil to dull redness had little effect on the solubility of the potassium.

Ethyl acetate and ammonia have practically no effect on the solubility, but water containing 2 per cent. of sugar or acetamide dissolves more potassium compound than pure water. Water saturated with carbonic anhydride dissolved 0·198 gram per litre; water containing 2 per cent. of acetic acid dissolved 0·290 gram per litre; water with 2 per cent. of hydrochloric acid 0·404 gram; water with 2 per cent. nitric acid 0·296 gram. These results afford no definite evidence either as to the forms in which the potassium exists in the soil or as to the proportion assimilable by plants.

Concentrated hydrochloric and nitric acids at a higher temperature dissolve considerably more potassium, the exact quantity depending on the temperature and time of action. The whole of the potassium, however, is never removed. Calcination of the soil increases the proportion of the potassium soluble in acids, probably in consequence of some alteration of the silicates.

It is not possible to draw any sharp line of demarcation between the potassium which is soluble or insoluble, assimilable or non-assimilable.

In order to obtain similar information respecting the potassium present in living plants, *Mercurialis annua* was selected as an example. The dried plant contained per kilo. 19·35 grams of nitrogen and 27·87 grams of potassium oxide, and left 125 grams of ash.

When treated with 10 times its weight of water for 24 hours, 18·92 grams of potassium per kilo., or two-thirds of the total amount, was dissolved. Hydrochloric acid of 2 to 3 per cent. dissolved 24·58 grams of potassium in 24 hours, or 5·66 grams more than water. The remaining 3·29 grams was present in some form insoluble in dilute acids.

A sample of vegetable mould which was examined in a similar way contained 32·4 per cent. of water and lost 45·9 per cent. when calcined in presence of air. The dried mould contained per kilo. 95·8 grams of organic carbon; 14·5 grams combined carbonic anhydride; 8·6 grams of nitrogen; and 11·65 grams of potassium. 2·96 grams or one-quarter of the potassium was soluble in water; 5·84 grams was soluble in hydrochloric acid of 2 per cent., but even after incineration the quantity of potassium insoluble in acids was 2·14 grams per kilo. The proportion soluble in water was considerably less after incineration, owing doubtless to the action of the silicates on the potassium carbonate.

It is evident that the mould does not retain the whole of the potassium present in the original plant, a considerable proportion being removed by rain during the process of decay. The proportion remaining is, however, still much more considerable than in the soil, and mould is a truly complementary manure intermediate in its character between the organic and inorganic manures. C. H. B.

Best Time for Ploughing Yellow Lupines under. By BAESSLER (*Bied. Centr.*, 1887, 615—618).—The periods into which the growth of the yellow lupine which was to be used as "green manure" was divided, were (1) full bloom of main stem, (2) commencement of podding of the same, (3) full bloom of side shoots, (4) full ripeness of the pods of main stem. It was found that the plants should be ploughed under in the fourth period, for then they would give to the morgen N 140·3 kilos., K_2O 53·96, and P_2O_5 25·7, when 253,440 plants are allowed per morgen; at this period, the nitrogen and phosphoric acid are three times and the potash twice that found in the plant in the period of bloom. E. W. P.

Analysis of Rubbish-heaps employed to Improve Soils. By A. MAYER (*Bied. Centr.*, 1887, 577—578).—The rubbish-heaps are found at places of refuge which were frequented in times of flooding before Holland was protected by dykes; they consist largely of animal and vegetable remains. The analysis of one sample must here suffice: Organic matter, 6·0 per cent.; total nitrogen, 0·14; easily soluble nitrogen, 0·02; phosphoric acid, 0·78; potash, 0·34; calcium carbonate, 1·1. The material is richer in plant food than the various "muds" used for amelioration of poor land; in the former, the lowest quantity of phosphoric acid is higher than the highest percentage in the latter; the same may be said for potash and nitrogen, but the muds contain more calcium carbonate.

E. W P.

Analytical Chemistry.

Support for Funnels while Drying. By V. Meurer (*Zeit. anal. Chem.*, **26**, 614).—Two horizontal, parallel bars of glass tube are supported by pieces of glass rod, which have their ends bent upwards till they nearly meet, and thrust into the ends of the tubes which are bent downwards at right angles. A small hook of glass rod prevents the bars from springing apart under the weight of the funnels which rest between them. M. J. S.

Moisture remaining in a Gas after drying by Phosphoric Anhydride. By E. W. Morley (*Amer. J. Sci.*, **34**, 199—204).—The method employed for determining the amount of aqueous vapour left in a gas after drying with phosphoric anhydride, consists in drying the gas with that substance, and then passing it through a weighed apparatus in which the gas is first slightly moistened, then much expanded, and, lastly, again dried by phosphoric anhydride. The decrease in weight of the apparatus is then due to the moisture left by phosphoric anhydride in that volume by which the gas passing out of the apparatus exceeds the gas entering it. In this way, it was found that the moisture left unabsorbed may be roughly estimated at a fourth of a milligram in 10,000 litres of gas. (For the result with sulphuric acid see Abstr., 1886, 278.) B. H. B.

Hygienic Air Analysis. By K. Sondén (*Zeit. anal. Chem.*, **26**, 592—598).—The apparatus is essentially that of Pettersson (Abstr., 1887, 999; also 179 and 180), but with the inlet tube so arranged as to draw the sample of air for analysis from a pipette in which it has been collected, thus avoiding the necessity of performing the analysis in the locality from which the air is taken. The carbonic anhydride only is determined, the gases being saturated with moisture before each measurement. Results agreeing closely among themselves and fairly with determinations by Pettenkofer's method have been obtained with an apparatus containing only 18 c.c. of air. M. J. S.

Estimation of Sulphurous Acid by Standard Iodine Solution. By J. Volhard (*Annalen*, **242**, 93—113).—The drawback to Bunsen's volumetric method, involving the use of standard iodine solution and dilute sulphurous acid, is the fact that the acid solution will not be completely oxidised if it contains more than 0·04 per cent. of SO_2. The incomplete oxidation of the sulphurous acid in stronger solutions is generally attributed to the action of the sulphuric acid on the hydriodic acid:—$H_2SO_4 + 2HI = I_2 + H_2SO_3 + H_2O$. The author finds that the true explanation is, that sulphurous acid is decomposed by a strong solution of hydriodic acid, yielding sulphur and iodine; the iodine at once oxidises sulphurous acid to sulphuric acid and is itself converted into hydriodic acid; this secondary action may be avoided by adding the moderately dilute sulphurous acid to the standard iodine solution. W. C. W.

Rapid Method of Determining the Total Acidity in Flue Gases from Vitriol Chambers, adapted for the use of Workmen. By W. YOUNGER (*J. Soc. Chem. Ind.*, 6, 347—348).—The author recommends the use of Hurter's apparatus, which is described in detail in Wanklyn's book on "Gas Analysis." The method being intended only for the use of foremen, to serve as a guide in the working of chambers, no pretensions are made to any great degree of accuracy. The most useful property of the apparatus is that it indicates how far the combustion is carried on, what fuel is used, and how much is wasted.

D. B.

Soda-lime Method for Determining Nitrogen. By W. O. ATWATER and C. D. WOODS (*Amer. Chem. J.*, 9, 311—324).—The soda-lime is prepared by slaking 2½ kilos. of lime in an iron kettle with a solution of 1 kilo. of sodium hydroxide, evaporating, and heating to fusion. It is ground whilst warm, and divided into two portions by sieves of ¾ mm. and 2 mm. This soda-lime is, on the whole, preferable to a more fusible one containing more soda, the complete decomposition of the substance being effected by the large surface presented by the coarse soda-lime with which the front part of the tube is filled. The same results are obtained whether the lime contains much or little soda, or even none, the ammonia probably being produced by the action of superheated steam. Combustions with sugar are not to be recommended for testing the purity of soda-lime, as even when recrystallised from alcohol it appears to contain a trace of nitrogen; stearic acid or oxalic acid is to be preferred. For the filling of the absorption-bulb, it is convenient to have a little thistle funnel blown on the end of the exit tube. If the tubes are well and closely packed with granular soda-lime, so as to leave no considerable open channel, and if a sufficiency of powdered soda-lime be well mixed with the substance, short tubes, 30 cm. long, may be used; cochineal is used as indicator.

When using the absolute method for the determination of nitrogen, a small correction should be made for the residual air and for the vapour-tension of the potash solution, namely, when at sp. gr. 1·36, 4 mm. at 9·5° and 6·5 mm. at 14·5°.

Although the results obtained by the two methods are almost the same, the soda-lime method is not quite so exact, but is much simpler, and sufficient for most purposes if the above precautions are observed.

H. B.

Determination of Nitrogen by Kjeldahl's Method. By L. LENZ (*Zeit. anal. Chem.*, 26, 590—592).—To ascertain whether the addition of permanganate is invariably necessary, comparative determinations were made on 11 nitrogenous substances, containing from 1·4 to 14 per cent. of nitrogen. In every case, the use of permanganate gave the higher result, the difference varying from 0·28 to 16 per cent. of the whole. The permanganate cannot, therefore, in any case be safely dispensed with. M. J. S.

Apparatus for Nitric Acid Determination. By KRATSCHMER (*Zeit. anal. Chem.*, 26, 608—610).—A simple apparatus for Schlösing's method. A flask of 150 c.c. capacity is fitted with a caoutchouc stopper, through which pass the tube of a separator bulb with a good stopcock and a long (3 to 4 dcm.) delivery tube bent downwards at an acute angle and turned up at the end. The nitrate solution is boiled in the flask (the delivery tube dipping into the mercury trough) until every trace of air is expelled. The stopcock is then closed, a boiling hot mixture of ferrous chloride and hydrochloric acid is poured into the bulb, and the lamp is removed. As soon as the mercury begins to rise in the delivery tube, the ferrous solution is allowed to flow in, the lamp is replaced, and the nitric oxide boiled out as usual. A little of the ferrous solution should remain in the bulb to act as a seal. M. J. S.

Determination of Phosphoric Acid. By A. Isbert and A. Stutzer (*Zeit. anal. Chem.*, **26**, 583—587).—The method based on the determination of the ammonia in the phosphomolybdate precipitate (Abstr., 1887, 526) is confirmed. A further simplification consists in washing the yellow precipitate with cold water instead of with ammonium nitrate solution. The compound of silicic acid with ammonia and molybdic acid is soluble in pure water although insoluble in ammonium nitrate. On the other hand, the phosphomolybdate requires 10,000 parts of cold water for its solution. The removal of silica by evaporation may therefore be omitted. The precipitate is allowed to subside completely at 70°, and filtered off after cooling. It is thrown with its filter into a flask, and distilled with soda into standard acid, which is then titrated back with baryta, using corallin as indicator. One part of nitrogen in the precipitate corresponds with 1·654 parts of phosphoric anhydride. Test analyses with known quantities of phosphate, with and without silicic acid, and comparative assays of phosphatic manures by the above and the gravimetric process, show that for commercial purposes the method is sufficiently accurate. M. J. S.

New Methods of Estimating Arsenic in Pyrites. By J. Clark (*J. Soc. Chem. Ind.*, **6**, 352—355).—*Precipitation Process.*—Three grams of the finely powdered pyrites is mixed in a platinum crucible with four times its weight of calcined magnesia and soda, and the mixture heated for about 10 minutes over a moderately low Bunsen flame. The contents of the crucible are then extracted with boiling water and filtered. The filtrate, which should be green in colour owing to the presence of iron, is acidified with hydrochloric acid, and the solution, which is now nearly colourless, is boiled for a few minutes, when the arsenic sulphide will separate along with sulphur. To ensure complete precipitation of the arsenic, it is always advisable to saturate the solution with hydrogen sulphide. The precipitate is then thrown on to a filter, washed, dissolved with ammonia, and the solution evaporated to dryness on a water-bath. The residue is treated with nitric acid and the arsenic in the solution either estimated as magnesium ammonium arsenate, or precipitated as silver arsenate, and the arsenic calculated from the silver as determined volumetrically by Volhard's process, or gravimetrically by cupellation, as recommended by Richter.

Distillation Process.—About 1·7 gram of the finely pulverised pyrites is introduced into a platinum crucible with six times the weight of the above mixture, and heated for an hour over a low Bunsen flame. The contents of the crucible are transferred to a flask, moistened with water, and dissolved in strong hydrochloric acid. The flask, which is fitted with a funnel tube, having the end drawn to a point and dipping under the liquid, is then connected with a small glass condenser, to the end of which a straight calcium chloride tube is attached, and by means of the funnel tube a considerable excess of cuprous chloride dissolved in strong hydrochloric acid is introduced. The contents are then slowly distilled into water for an hour, when a fresh quantity of hydrochloric acid is introduced, and the distillation continued for ½ hour. The whole of the arsenic will now be found in the receiver, but it is always advisable to add a little more hydrochloric acid, change the receiver, and test the distillate. The arsenic is then precipitated as sulphide, or it is titrated with iodine in the usual way. D. B.

Estimation of Silicon in Iron and Steel. By J. J. Morgan (*Chem. News*, **56**, 221).—The author criticises Turner's statements (Abstr., 1887, 1140), and states that silica may be obtained free from iron and phosphorus in the following manner:—The solution obtained by dissolving iron in *aqua regia* is evaporated to a thick syrupy consistence, treated with hydrochloric acid, and the precipitated silica well washed with dilute hydrochloric acid and water, when it is found to be free from both iron and phosphorus. D. A. L.

Estimation of Silicon in Iron and Steel. By T. Turner (*Chem. News*, **56**, 244—245).—A reply to Morgan (preceding Abstract). Whilst the process described above will give fairly accurate results with iron containing under 1 per cent. of phosphorus and about 1 per cent. of silicon, this is not the case with commoner irons containing 2 per cent. of phosphorus and 3 to 4 per cent. of silicon.

Indirect Determination of Alkalis in Presence of Lithium. By K. Kraut (*Zeit. anal. Chem.*, **26**, 604—605).—The metals are weighed as nitrates, and the nitric anhydride then expelled by fusion with silica. The calculation is made in the usual manner.

Chlorides are converted into nitrates by treatment with silver nitrate. Phosphates are dissolved in a little nitric acid, about an equivalent quantity of silver nitrate is added, and then freshly precipitated silver oxide to neutrality. The excess of silver in either case is removed from the filtrate by hydrocyanic acid. This method is not applicable to sulphates, since barium sulphate cannot be freed from lithium salts by washing. M. J. S.

Determination of Ammonia in Commercial Products. By J. M. Milne (*J. Soc. Chem. Ind.*, **6**, 423).—Some time ago a German committee recommended the liberation of the ammonia from phosphates, manures, and other commercial products, by boiling with magnesia instead of alkaline hydroxides, and absorption in a measured excess of standard sulphuric acid. One great advantage of this modification is that the contents of the distilling flask boil quite quietly, and can be brought nearly to dryness without spirting if the gas flame is properly regulated. The author has used this method for some time with very satisfactory results. It is necessary, however, to observe the following precautions:—(1) The steam containing the ammonia should be thoroughly condensed as it passes over. (2) The end of the condenser tube should not dip beneath the surface of the sulphuric acid in the bulb flask. (3) In order to ensure complete absorption of the ammonia, a small U-tube containing a little of the standard acid should be attached to the exit tube of the flask.

D. B.

Assay of Silver containing Small Quantities of Bismuth. By J. Scully (see p. 108).

Estimation of Mercury in Urine. By L. Brasse (*Compt. rend. Soc. Biol.* [8], **4**, 297—300).—Simple electrolysis is insufficient, inasmuch as certain organic matters are deposited along with the mercury on the electrode. To obviate this error, the author treats 100 c.c. of urine with 10 c.c. of hydrochloric acid, places in the mixture a small coil of thin sheet brass 1 cm. broad by about 50 cm. long, and allows the interaction to go on for a day. The coil is then removed, washed with alcohol and ether, dried, transferred to a porcelain crucible and heated. The mercury vapour is condensed on a concave cover of gold kept cool by distilled water. The difference between the weight of the dried cover before and after heating gives the amount of mercury. J. P. L.

Estimation of Iron in Chars. By R. Davidson (*J. Soc. Chem. Ind.*, **6**, 421).—Having tested the accuracy of the stannous chloride process for the estimation of iron in the case of substances such as animal charcoal, containing only from 0·1 to 1·0 per cent. of ferric oxide, the author confidently recommends it in preference to either the "permanganate" or "dichromate" process. D. B.

Determination of Ferrous Oxide in Insoluble Silicates. By A. H. Chester and F. I. Cairns (*Amer. J. Sci.*, **34**, 113—116).—In their examination of the crocidolite from Rhode Island, the authors determined the ferrous oxide by means of ammonium fluoride. Half a gram of the pulverised mineral is placed in a large platinum crucible over a water-bath, and a slow stream of carbonic anhydride is carried into it. When the air is expelled, a few drops of concentrated sulphuric acid is added, then some ammonium fluoride. Similar additions are made from time to time until the mineral is completely decomposed. The contents of the crucible are then emptied into a beaker containing cold water. The solution is diluted, and the iron determined by means of potassium permanganate in the usual manner.

B. H. B.

Estimation of Titanic Oxide. By L. Lévy (*Compt. rend.*, **105**, 754—756).—The author has investigated the conditions necessary to ensure accuracy when using the ordinary method of fusing with potassium hydrogen sulphate, extracting with water, and precipitating the titanic oxide by prolonged boiling. The solution should contain 0·5 per cent. of free sulphuric acid; if less, the precipitate is impure; if more, precipitation is incomplete. The presence of zinc in the solution is without influence on the result, provided the proportion of free acid is 0·5 per cent., and the same is true of copper, magnesium, and aluminium, but in presence of ferric sulphate the result is always too high.

The best method of procedure is as follows:—The fused mass is mixed with sufficient sulphuric acid to convert the whole of the potassium into the hydrogen sulphate, solution being thus greatly accelerated, and the liquid is then carefully neutralised with potassium hydroxide, free sulphuric acid added to the extent of 0·5 per cent., and the solution boiled for six hours. C. H. B.

Determination of Antimony. By F. MUCK (*Zeit. anal. Chem.*, **26**, 600—602).—The precipitate of trisulphide is dried by suction until it can be detached from the filter. The filter is washed with warm ammonium sulphide in which much free sulphur has been dissolved, this polysulphide having a far greater solvent action than the monosulphide. The solution is evaporated in a porcelain crucible. A convenient way of doing this is to support the crucible on a glass triangle in a deep glass basin containing a little sulphuric acid, and covered closely with a glass plate. On gently heating the basin on a bed of asbestos, the liquid evaporates rapidly without spitting. The detached precipitate is then added and the whole dried. The free sulphur is removed by treatment with a mixture of carbon bisulphide and chloroform, and the antimony sulphide is converted into tetroxide for weighing. M. J. S.

Delicate Test for Bismuth. By F. B. STONE (*J. Soc. Chem. Ind.*, **6**, 416).—This test depends on the fact that a strong solution of potassium iodide produces a bright yellow colour when added to a very dilute solution of bismuth sulphate containing only a small quantity of free sulpuric acid. 1 part of bismuth oxide in 1,000,000 parts will show a distinct coloration. Very small quantities of bismuth may also be estimated colorimetrically by means of this test. D. B.

Detection of Nitrates in Well Water. By O. BINDER (*Zeit. anal. Chem.*, **26**, 605—606).—The method depending on the reduction to nitrite by zinc, and testing with potassium iodide and starch, fails if too much zinc is used. A trace of zinc powder shaken with the liquid answers better than compact zinc. M. J. S.

Water Analysis. By O. BINDER (*Zeit. anal. Chem.*, **26**, 607).—Liquids, such as natural waters, evaporated over a free gas flame, become contaminated with sulphuric acid from the products of combustion. M. J. S.

Elementary Analysis of Highly Volatile Organic Liquids. By G. KASSNER (*Zeit. anal. Chem.*, **26**, 588—590).—The combustion tube is prolonged at the posterior end beyond the furnace, and is bent upwards at an angle of about 45°. A plug of asbestos is placed at the bend. The bulb containing the liquid is introduced at this end, and rests against the asbestos plug with its capillary tube pointing upwards. The bulb having been cooled before breaking the point of the capillary tube, can be introduced without the escape of any of the liquid, and the gradual expulsion of the contents can be watched and regulated, since the vaporised liquid condenses in the capillary tube, and is driven out in the form of minute drops. These are immediately evaporated and swept forward by the current of oxygen passed through the tube. The more volatile the liquid, the longer and narrower should be the capillary tube. The portion of the combustion tube which is to be heated is filled with platinised asbestos (see Kopfer, *ibid.*, **17**, 1). For substances which burn with difficulty, however, cupric oxide cannot be dispensed with. For arresting halogens, a plug is employed prepared by shaking chopped asbestos with finely divided, reduced silver. A stream of hydrogen (free from arsenic or antimony) passed through the hot tube regenerates the metallic silver after it has absorbed a halogen. M. J. S.

The Stalagmometer. By J. TRAUBE (*Ber.*, **20**, 2824—2835).—Applications of the stalagmometer (this vol., p. 91) to the estimation of alcohol in wine, beer, and liqueurs, and of acetic acid and alcohol in vinegar. Tables are given for use at temperatures between 10° and 30° for alcohol, and 11° and 29° for acetic acid, for percentages up to 10 per cent. by weight of the pure substance in each case.

W. P. W.

Recognition of Pyrogallol. By G. KLIEBAHN (*Zeit. anal. Chem.*, **26**, 641).—Pyrogallol when fused with ammonium oxalate yields ammonium rufigallate, which dissolves in water with red colour, and gives the following characteristic reactions:—Potassium ferricyanide and potassium dichromate, a dark-brown precipitate insoluble in alcohol. Ferric chloride, no black coloration. A few drops of acetic acid, then potassium cyanide and mercurous nitrate, a black precipitate. Sodium nitroprusside and platinic chloride, no precipitate or change of colour. Potash, a change to brown, but not to black.

M. J. S.

Estimation of Grape-sugar in Urine by Robert's Method. By V. BUDDE (*Pflüger's Archiv*, **40**, 137—172).—The fermentation method of determining the amount of sugar in diabetic urine consists in multiplying the difference in specific gravity before and after removal of the sugar by fermentation, by a constant factor found by control titration experiments in which the percentage so found was divided by the difference in the specific gravities. Worm-Müller has stated (*ibid.*, **37**, 479—510) that this factor is constant, namely, 230. This paper is devoted to showing mathematically that from its very nature this factor is a variable one, increasing as the percentage of sugar diminishes. W. D. H.

Examination of Wort and Starch. By E. W. T. Jones (*Analyst*, **12**, 163—168).—The methods employed are essentially those described by O'Sullivan (this Journal, 1876, ii, 130). An analysis is given of a wort which gave $[\alpha]_{j\,3\cdot86} = 116\cdot5$, and $K = 50\cdot8$ (Trans., 1879, 606). The same wort analysed in the Inland Revenue Laboratory gave the values $[\alpha] = 120$, and $K = 57\cdot2$, on which numbers a charge of the addition of 1·6 per cent. of glucose was based. The suggestion is made that the higher value of K may have been obtained by the use of Fehling's solution volumetrically in the presence of dextrin. On keeping this wort for four months (after adding salicylic acid). the rotatory power diminished, whilst the cupric reducing power increased. Some of the same malt, mashed in the laboratory for three hours at 57—60°, gave $[\alpha] = 113\cdot6$, $K = 51\cdot85$, from which it would appear that with some malts the limits recognised by the Inland Revenue chemists ($[\alpha]$ not less than 120, and K not over 51) may be exceeded.

The method of analysing starch differs from that of O'Sullivan (Trans., 1884, 9) only in the omission of the washings with ether, alcohol, and warm water before gelatinising, and in controlling the results of the optical method by a subsequent hydrolysis with acid, and a determination by Fehling's solution. M. J. S.

Estimation of Small Quantities of Lactic Acid. By W. Windisch (*Chem. Centr.*, 1887, 826, from *Wochenschr. f. Braueri*, **13**, 214).—In order to estimate small quantities of lactic acid, the substance to be examined is heated with chromic acid, whereby the lactic acid is decomposed into formic acid and aldehyde. The mixed vapours are passed into Nessler solution, in which, in presence of an aldehyde, lead salts give a yellowish-red precipitate, or with smaller quantities, a yellowish opalescence. In order to examine roots by this process, they are first extracted with ether, which dissolves out all acid substances. V. H. V.

New Method of Examining Butter. By T. T. P. B. Warren (*Chem. News*, **56**, 222, 231, 243—244).—Five grams of butter is placed in a tared tube, plugged with asbestos, and is extracted with carbon bisulphide. The fats are weighed, dissolved in carbon bisulphide, and well mixed with a solution of equal volumes of yellow sulphur chloride and carbon bisulphide; the latter is evaporated, and the thickened mass redissolved in carbon bisulphide, any insoluble residue indicating the presence of vegetable oils. The filter tube is dried and weighed; then by successive weighings after washing, first with water, then with ammonia, the dry matter, soluble substances, caseïn, &c., are determined. The sulphur chloride treatment applied to other fatty mixtures, such as lard, oil, or oleomargarin, will detect the admixture of any vegetable oil, rosin, rosin oil, or petroleum. After a few hours' contact with sulphur chloride, butter becomes brownish, commercial oleïn thickens and turns black, and animal oleïn assumes a very dark colour, but all dissolve in carbon bisulphide, whereas vegetable oils do not. Inasmuch as animal oils themselves dissolve vegetable oils, a small quantity of the latter might escape detection in presence of a large quantity of the former; to avoid this it is suggested to add to the butter or other fatty mixture sufficient tested cotton-seed oil to supersaturate the animal fats; then by treatment with sulphur chloride and subsequent washing with carbon bisulphide, the animal fats are removed, and the vegetable oils remain insoluble. Any excess residue over that due to the cotton-seed oil added is derived from vegetable oil, present in the butter; this is, however, only approximately quantitative. Water must be absent when using sulphur chloride. Other precautions are noted, and some remarks are advanced on the character of the reaction of sulphur chloride on fats, and of the products formed in the reaction. Attention is drawn to the high percentage of caseïn in some samples of country butter, probably indicating the use of this substance as an adulterant. D. A. L.

The Reichert-Meissl Process for the Estimation of Butter Fat. By R. WOLLNY (*Bied. Centr.*, 1887, 699—703).—Errors frequently arise in the results obtained by working this process, the results being generally too high. This the author ascribes to the presence of carbonates in the potash used for saponification. A loss may also occur from the fact that distillation with sulphuric acid in presence of alcohol will produce ethereal salts of butyric and other acids, consequently the results may be too low. If the following precautions are taken, the results will be accurate. Instead of potassium hydroxide, a 50 per cent. sodium hydroxide solution is to be used, and allowed to settle before putting aside. Admission of carbonic anhydride to the saponifying solution must be avoided, and for this purpose the saponification must be conducted in a vessel to which a reflux condenser is attached, and the distillation of the alcohol should be effected without opening the apparatus. A closed ⊤-tube is inserted between the flask and condenser, whereby, after distillation, water and acid can be added. As regards the process itself, 5 grams of the molten and filtered fat is accurately weighed into a 300 c.c. flask (length of neck 7 to 8 cm.), 2 c.c. of 50 per cent. sodium hydroxide solution, which has been preserved from all contact with carbonic anhydride, and 10 c.c. alcohol (96 vol. per cent.) are introduced into the flask, and after connection with the reflux condenser the flask is heated in the water-bath for ¼ hour; the alcohol is distilled off, and the heat continued for at least ½ hour, 100 c.c. distilled water is then added, and the mixture further heated for ¼ hour, until the soap is dissolved. The clear solution is now to be decomposed whilst hot by 40 c.c. of sulphuric acid (30—35 c.c. = 2 c.c. of the soda solution), and a small piece of pumice should also be introduced. Distillation must be continued until 110 c.c. of the liquid has been collected, the distillate well mixed, and of it 100 c.c. filtered off and titrated with decinormal baryta, phenolphthaleïn being used as indicator. The figure thus obtained is to be multiplied by 1·1, and from the product are to be deducted such figures as are obtained from a preliminary blank experiment. The deduction to be made should not exceed 0·33.

E. W. P.

Examination of Cod-liver Oil and Vegetable Oils. By E. SALKOWSKI (*Zeit. anal. Chem.*, **26**, 557—582).—The determination of the temperature of solidification is of little assistance, since undoubtedly genuine specimens show widely different solidifying points. Moreover, cod-liver oil solidifies with extreme slowness, even at temperatures far below its freezing point, and an admixture of 20 per cent. of rape-seed, linseed, or cotton-seed oil, with an oil of low freezing point is not revealed at a temperature (0° C.) at which other genuine oils solidify. The presence of palm oil, palm kernel oil, or cocoa-nut oil may, however, be suspected if solidification occurs in 15 to 30 minutes at 0°.

Treated by Reichert's process, cod-liver oil gives a very small quantity of volatile acid. Linseed, rape-seed, cotton-seed, and palm oils give a slightly higher yield, but not sufficiently different to enable this method to detect an admixture.

When cod-liver oil is saponified and the dilute solution of the soap shaken with ether, cholesterin is extracted, together with a yellow substance, which seems to belong to the lipochrome series (Kühne, *Untersuch. physiol. Inst. Heidelberg*, 1882). This substance gives an indigo-blue colour with strong sulphuric acid, whilst cholesterin and also the cod-liver oil itself give violet. The fatty acids from the soap solution freed from cholesterin, when dissolved in chloroform and mixed with sulphuric acid, give a dark brown-red colour, with dirty-green fluorescence. If after pouring off the chloroform some of the acid is added to glacial acetic acid, the mixture slowly acquires a fine red-violet colour, with dirty-green fluorescence. The only vegetable oils which in choloform solution are coloured blue by sulphuric acid are palm oil and cotton-seed oil. All the vegetable oils (except palm oil), when treated as above for the extraction of cholesterin, yielded a substance which was identified with the phytosterin of Hesse. This may be distinguished from cholesterin by its appearance under the microscope. A hot alcoholic solution of cholesterin solidifies on cooling to a mass of thin, rhombic plates, frequently showing re-entering angles; the substance obtained from the vegetable oils forms stellate or fasciculate groups of thick needles, or on slow cooling gives elongated six-sided plates. The products from all the vegetable oils melted at 132—134° (Hesse's phytosterin at 132—133°). Cholesterin from genuine cod-liver oil melts at 146°; the product from an oil adulterated with 20 per cent. of rape, linseed, or cotton-seed oil melted at 139—140°, and showed the needles of phytosterin, together with the plates of cholesterin.

Most of the specimens of cod-liver oil examined contained very little free fatty acid (0·24 to 0·69 per cent. calculated as oleic acid; one specimen, however, showed 6·5 per cent.). Since many vegetable oils give numbers lying within these limits, this character is of no service for their detection. M. J. S.

Titration of Urea with Mercuric Nitrate. By E. PFLÜGER (*Pflüger's Archiv*, **40**, 533—586).—After some critical remarks on von Rautenberg's and Pfeiffer's modifications of Liebig's method of estimating urea, a series of 28 experiments is detailed, in which the amount of nitrogen in urine was estimated first by Kjeldahl's method, and secondly by Rautenberg's mercurial solution. In some cases, the results by the latter were higher, in others lower than by Kjeldahl's method, and taking Kjeldahl's method as one which gives accurate results, it is calculated that the average error of Rautenberg's method is 0·7 per cent. On the average, out of 100 parts of the nitrogen in urine, 13 are combined in substances other than urea. Rautenberg's method does not give the amount of urea, but the total nitrogen. W. D. H.

Fractional Reduction of Ortho- and Para-nitrotoluene and Quantitative Analysis of Ortho- and Para-toluidine. By T. Miniati, H. Booth, and J. B. Cohen (*J. Soc. Chem. Ind.*, 6, 418—420). —From a series of experiments on the reduction of ortho- and para-nitrotoluene, it seems that both nitro-compounds are acted on concurrently.

Before commencing their analytical work, the authors thought it desirable to determine whether the reduction could be so regulated that approximately the same quantities of nitrotoluene could be reduced with a given quantity of the reducing agent; it was found that with care this could be readily accomplished. The separation and isolation of the nitrotoluene and toluidine is effected in the following manner:—After reduction, the acid solution obtained is distilled with steam, and the unattacked nitrotoluene driven over, the toluidine remaining behind. The toluidine solution is freed from tin by treatment with hydrogen sulphide and filtered. The filtrate is made alkaline and distilled with steam, when the toluidine distils over. Both distillates are extracted with ether, the ether is distilled off and the residues dried and weighed. The first gives the weight of nitrotoluene, the second that of the toluidine. Having the respective weights, an analysis of the one or the other and determination of the quantity of ortho- and para-compound present therein, suffices to find exactly how the reduction has gone. Having made unsuccessful attempts to analyse the resulting nitro-compound, the authors tried various methods for the quantitative estimation of ortho- and para-toluidine. The only process they found practicable was to add excess of oxalic acid solution, bring the precipitate on to a filter-paper, wash three or four times with ether, and weigh on a watch-glass. Any residue remaining in the precipitating vessel and in the filter-paper was dissolved in water and titrated with decinormal potash solution. With paratoluidine, it was found that precipitation was not complete unless the mixture was allowed to remain 12 hours. With pure orthotoluidine, there is no immediate precipitation, but in 12 hours from 4 to 5 per cent. of the ortho-compound crystallises out; hence in performing the analysis the error due to the precipitation of the ortho-compound must be allowed for if the solution remains 12 hours, or the error due to incomplete precipitation of the para-compound must be allowed for if the precipitate is filtered immediately. The better plan would therefore be to obtain an approximation of the amount of para-compound present in one determination, and then run in just sufficient oxalic acid solution to precipitate this quantity, and wait for 12 hours. D. B.

Estimation of Small Quantities of Paratoluidine in Orthotoluidine. By C. HAEUSSERMANN (*Chem. Ind.*, **10**, 55—56).—Of the methods recommended for the estimation of para- and ortho-toluidine the process based on the titration of the para-compound with oxalic acid in an ethereal solution has been mostly adopted. It is not, however, wholly free from error, owing to the fact that the amount of ether to be used is frequently insufficient to completely dissolve the "ortho-oxalate" produced by the reaction. The author suggests the following method:—A solution containing 88 grams of crystallised oxalic acid in 750 c.c. of water and 43 c.c. of hydrochloric acid of 22° B. is heated in a porcelain basin to 70—75°, and treated with 10 grams of the toluidine under examination. When the precipitate which separates has been entirely redissolved, the mixture is allowed to cool gradually to 30—35° until the oxalate shows signs of crystallisation on the surface of the solution. It is then filtered through cotton and the residue washed with a few drops of water. The precipitate forms small, colourless scales having a dull appearance. The filtrate on standing deposits a further portion of crystals which are collected on a separate filter and washed. This operation is repeated until crystals are obtained having a lustrous appearance. These consist of the pure "ortho-oxalate," and are readily distinguished from the crystals of the para-compound. The crystalline fractions are then treated with a solution of sodium carbonate and subjected separately to distillation. The solidifying point of the distilled bases is determined by cooling a fraction of each distillate with ice. If the oil solidifies by merely agitating it, the crystals are collected on a tared filter, and after drying over sodium hydroxide weighed as paratoluidine. If, however, the addition of a few crystals of pure paratoluidine is required to induce solidification, only one-half of the mass is calculated as paratoluidine. If, on the other hand, it is impossible to solidify the base obtained from the distillation of the first crystalline fraction, orthotoluidine only is present in the sample under examination. With good toluidines, it generally suffices to collect and distil two fractions, in which case the base from the second crystallisation mostly constitutes a perfectly liquid oil. This method being inapplicable to mixtures containing more than 10 per cent. of paratoluidine, it is suggested to dilute such mixtures by the addition of pure orthotoluidine. D. B.

Volumetric Determination of Alkaloïds by Mayer's Reagent. By F. S. HERETH (*Zeit. anal. Chem.*, **26**, 647).—To avoid the errors introduced by the use of filters and the irregular addition of the reagent (potassio-mercuric iodide), several equal portions of the solution to be titrated should be mixed at once with quantities of the reagent differing from one another by 0·1 c.c., and ranging from somewhat below the amount indicated by a rough preliminary test to an equal distance above. After settling for at least eight hours in a closed test-tube, part of the clear upper liquor can be poured off and tested by a drop of the reagent. The extract is prepared for titration by acidifying and gently warming to drive off alcohol. If any precipitate separates it is filtered off and washed with dilute acid. The liquid should finally contain about 1 per cent. of free sulphuric acid.

M. J. S.

Tanret's Reaction for Albumin, Peptone, and Alkaloïds in Urine. By L. BRASSE (*Compt. rend. Soc. Biol.* [8], **4**, 369—370).—Albumin, peptone, and alkaloïds are precipitated from urine in the cold by Tanret's reagent, potassium mercury iodide. On heating, the peptone and alkaloïdal precipitate dissolves, leaving the albumin insoluble. The alkaloïdal precipitate can be easily separated from the peptone precipitate by reason of its solubility in ether.

No insoluble combinations are formed with any of the ordinary constituents of urine, such as creatine, creatinine, xanthine, or hypoxanthine, but bile salts give rise to a precipitate insoluble, like albumin, in both cold and hot solutions. This precipitate, however, can be differentiated from the ordinary albumin precipitate inasmuch as it is soluble in ether.

J. P. L.

Hæmatoscopic Study of Blood. By A. HÉNOCQUE (*Compt. rend. Soc. Biol.* [8], **4**, 283—284).—The chief advantage in the use of the hæmatoscope (Abstr., 1887, 312), for the spectroscopic examination of blood is the possibility of examining the blood undiluted.

J. P. L.

General and Physical Chemistry.

Chemical Action of Light on an Explosive Mixture of Chlorine and Hydrogen. By E. PRINGSHEIM (*Ann. Phys. Chem.* [2], **32**, 384—428).—Bunsen and Roscoe (*Ann. Phys. Chem.*, **96**, 373; **100**, 43, 481; **101**, 235; **108**, 193; **117**, 529) propounded the question—"Whether in photochemical combination an amount of work is done for which an equivalent of luminous energy disappears, or whether the action effected by the chemical rays is merely started by the light without the expenditure of a sensible amount of luminous energy." They endeavoured to solve this problem in the case of hydrogen and chlorine, by comparing the quantity of light absorbed by the mixture with that absorbed by dry chlorine, or as they call it, the optical extinction in chlorine. They assumed that this optical extinction would be of the same amount in the mixture, and therefore concluded that the considerable additional extinction observed in the mixture was due to the transformation of luminous energy into heat energy during the chemical action. The author objects to this reasoning, that the light absorbed in chlorine alone is itself transformed into heat, thereby raising the temperature of the gas, whilst in the case of the mixture, the luminous energy may very probably be transformed directly into chemical energy. In support of this view, he adduces Bunsen and Roscoe's observation that the action of light was considerable when the range of temperature was from 18° to 26°.

The luminous energy, indeed, may either increase the molecular motion directly and the atomic motion indirectly, or *vice versâ*, or more probably both processes may go on simultaneously. From the kinetic theory of gases, the introduction of energy by conduction of heat must increase the molecular velocities, which are of a very irregular character. Now it is found that the absorption of light is a function of the wave-length, and it therefore seems probable that the chemical action of light consists in the direct transfer of energy to the atoms, whose motions consist of vibrations of definite periods, and is therefore the direct cause of dissociation. When in equilibrium, there is a definite relation between the atomic and the molecular energy of a gas, and if this is disturbed by the absorption of light, there will be a change in the number of molecular impacts, and before a fresh state of equilibrium is attained, the direct increase in the atomic energy may be more or less expended; in the present case in effecting chemical change; in other cases, in producing fluorescence, phosphorescence, or electrical phenomena. The assumption, therefore, that what Bunsen and Roscoe call the optically absorbed light simply increases the temperature, and that the additional absorption due to the presence of hydrogen increases the chemical absorption, is not justifiable. If the light absorbed by the chlorine molecules in the mixture produces chemical action, this, as shown later, will probably consist in the formation of intermediate unstable products whose coefficient of absorption of light differs from that of the mixture of chlorine and hydrogen, so that "chemical extinction" must be regarded as the consequence rather than the cause of the chemical change. The existence of chemical extinction is therefore no criterion as to whether transformation of luminous into chemical energy takes place, so that Bunsen and Roscoe's method is incapable of solving the question proposed by them, but a result obtained in another portion of their researches, namely, that the chemical action is proportional to the intensity of the light, although not so applied by them, seems to give the required solution; for if the action of the light were simply to disturb a state of unstable equilibrium, the quantity of hydrogen chloride formed would be independent of the initial impulse. It must, therefore, be assumed that a definite absorption of luminous energy will take place for every molecule of hydrogen chloride formed, but it does not follow that more light must be absorbed than with the chlorine alone.

The determination of the cause of the increase of the extinction-coefficient, which may be due merely to a change in the condition of the mixture, leads to an investigation of the physical and chemical phenomena which accompany the formation of hydrogen chloride, and therefore to the consideration of "Photochemical Induction." Bunsen and Roscoe found that when light falls on a freshly prepared mixture, or on one which has been for a time in darkness after previous exposure to light, there is at first no appreciable formation of hydrogen chloride; after a certain interval, a slight action begins, gradually increases to a maximum, and then remains constantly proportional to the time. The act of overcoming the resistance here indicated and bringing the gas into a state of readiness for combination, they call chemical induction, and when due to the action of light, photochemical induction. They found the duration of the seemingly inactive interval to increase with the thickness of gas traversed by the light, and to decrease with increasing intensity of light more rapidly than the intensity increases. Both of these results are confirmed by the author, who further finds that the rate of formation of hydrogen chloride depends only on the intensity, and not on the wave-length of the light, from which he concludes that the inductive action is probably a chemical one. By instantaneous exposure to a stronger source of light, he finds that the gas undergoes a momentary expansion proportional to the intensity of the light, which is evidently not due to the heat of formation of hydrogen chloride, from the rapidity with which it appears and disappears, and also because it is found to be independent of previous induction and of the amount of hydrogen chloride formed. Neither can it, for the former reason, be due to the heat which Budde (*Ann. Phys. Chem.*, **144**, 213) has shown to be produced by the absorption of light by chlorine.

He therefore concludes that some intermediate product is formed, that the expansion is due to momentary dissociation, and that the quantity formed is proportional to the intensity of the light. It does not seem reasonable to suppose that this may consist of molecules of H_2Cl and Cl or HCl_2 and H; the author therefore seeks for the cause in the presence of water-vapour (the gas being in contact with water during the experiments), in accordance with the influence known to be excited by water-vapour on other explosive mixtures, and in confirmation of this he finds that when a solution of hydrogen chloride is substituted for the water, and the gas dried as completely as possible, much less hydrogen chloride is formed by the action of light of given intensity, and with the feeble light used in the earlier experiments, no action at all takes place.

The author assumes the action to take place in two stages, for example:—

$$(1.)\ H_2 + Cl_2 + H_2O = Cl_2O + 2H_2;$$
$$(2.)\ Cl_2O + 2H_2 = 2HCl + H_2O;$$

or some similar action, the exact nature of which may be determined by chemical analysis. He supposes the action to be somewhat as follows:—The intermediate substance is first formed, the process continuing until a certain proportion of the gas is transformed. Mass actions then come into play between chlorine, hydrogen, water and the intermediate product, and hydrogen chloride begins to be formed. The second stage of induction now begins. The amount of the intermediate product increases more rapidly than it is used up in forming hydrogen chloride, which is therefore formed at an increasing rate, until the intermediate product is destroyed as fast as it is produced, introducing the third stage, in which the formation of hydrogen chloride is proportional to the time. When removed from the action of light, the quantity of intermediate product will soon fall below the minimum required for the production of hydrogen chloride, and the remainder will break up again into hydrogen, chlorine, and water. This gradual decomposition of the intermediate product into its original constituents will go on even during induction, which explains why, with diminishing intensity of light, the duration of induction increases more rapidly than the intensity diminishes, for since the nature of the change undergone by the intermediate product depends on its actual amount, therefore the less the intensity the greater will be the ratio of the amount destroyed to that newly formed in each moment. G. W. T.

Anomalous Dispersion produced by Glowing Vapours. By A. Winkelmann (*Ann. Phys. Chem.* [2], **32**, 439—442).—Kundt (*Ann. Phys. Chem.* [2], **10**, 231) discovered the anomalous dispersion produced by sodium vapour. The method he used was to allow a ray of light to pass through the conical flame of a Bunsen burner coloured with sodium vapour, so as to be refracted by the flame, which acted like a prism with its refracting angle horizontal and upwards, and then through a vertical prism, by which means he obtained crossed spectra which showed the anomalous dispersion. In the hope of making the action stronger, Kundt attempted, but without success, to reduce the flame to a prismatic form by the use of glass or mica plates. The author has succeeded in doing this by using as the burner a tube of triangular section and provided with an air-blast.

On the top of the tube is placed a double thickness of wire-gauze, and on that again a triangular support smaller than the section of the burner, made of iron wire, which carries an iron cup of the same dimensions as the support, in which the sodium is placed.

With this apparatus Kundt's phenomenon was exhibited very clearly, and it was also obtained, although less distinctly, with potassium. Lithium and thallium chlorides were also tried but with negative results; this the author attributes to the insufficient density of the vapour. G. W. T.

Components of the Rare Earths yielding Absorption-spectra. By G. Krüss and L. F. Nilson (*Ber.*, **20**, 3067—3072).—A reply to G. H. Bailey (this vol., p. 1), in which the authors maintain the correctness of their views on the components of the rare earths (Abstr., 1887, 890).

Components of the Rare Earths yielding Absorption-spectra. By G. H. Bailey (*Ber.*, **20**, 3325—3327).—A rejoinder to the preceding Abstract.

Theory of Researches on Contact-electricity. By F. Exner (*Ann. Phys. Chem.* [2], **32**, 515—520).—The author's recent researches in support of his denial of contact-electrification (*Ann. Phys. Chem.* [2], **32**, 53) were founded on his experimental result, that if an insulated conductor is connected with an electrometer, and the latter then disconnected from the earth, and if the capacity of the conductor is then altered, the electrometer will remain unaffected, whilst according to the contact-theory there should be a flow of electricity.

The present note is a reply to objections which Hallwachs (*ibid.*, 64) has advanced against the author's conclusions.

In reply to these objections he states that—

(1.) The potential of the grating of oxidised iron which surrounded the apparatus differed by less than 0·05 of a Daniell from that of the walls of the room, which would justify his neglecting it; moreover, from (4), its potential, whatever its value, would be without influence on the results.

(2.) The capacity of the conductor was measured inside the grating, and not outside as assumed by Hallwachs.

(3.) He is justified in neglecting the change of capacity in the quadrants during the movement of the needle, since for the maximum deflection to be expected the error so arising would not exceed 1 per cent., and as no deflection was observed, the objection is entirely irrelevant.

(4.) The potentials would naturally be understood to refer to that of the grating as zero, without an express statement to that effect; moreover, the author shows by a simple mathematical proof that the result is independent of the absolute values of the potential, the essence of his method consisting in eliminating the influence of the grating by comparative observations on different metals. The difference of deflections which should have been obtained according to the contact-theory would have amounted to from 10 to 15 scale-divisions, and would therefore be easily observed.

(5.) To eliminate the possibility that the absence of a deflection might be due to unknown external effects, a Daniell's cell was introduced into the insulated system, and the deflection obtained was found to agree closely with the value predicted theoretically.

(6.) The author claims that he has proved that no change is produced when the grating is brought into contact with a conductor consisting of a different metal. Such a change is required by the contact-theory, but the author has not attempted to determine whether it would be required by the chemical theory, nor, as far as he is aware, has the question been considered by others. G. W. T.

Resolution of the Electromotive Forces of Galvanic Elements into their Differences of Potential. By J. MOSER (*Monatsh.*, 8, 508—509.)—Examples are given in this paper of the resolution of the electromotive forces of certain galvanic combinations, and determination of each of the components at the electrolytic surface. The sum of these several components is shown to be equal to the total electromotive force of the cell. The method of "drop electrodes," as applied by the author to exclude the electromotive force of contact metals, is used, a method based upon an observation of Helmholtz, that if an insulated mass of mercury, dropping quickly, is in contact with an electrolyte at the dropping point, there is no difference of potential between the mercury and the electrolyte.

Thus the total electromotive force of the combination Zn | dilute $ZnCl_2$ | concentrated $ZnCl_2$ | Zn = 0·15 volt. The values of the electromotive force at the three surfaces v, f, and c, were found by the drop electrode method to be—

$$\begin{aligned} v &= 1{\cdot}1 \text{ volt} \\ c &= 0{\cdot}98 \text{ and } f = 0{\cdot}27 \\ f + c &= 0{\cdot}95. \end{aligned}$$

Now 1·1 − 0·95 = 0·15, or the value found for the total electromotive force.

Again taking the Daniell's cell as another example—

$$\left.\begin{array}{l|lr} \mathrm{Zn} & \mathrm{ZnSO_4} & = 198 \\ \mathrm{Zn} & \mathrm{ZnSO_4} \mid \mathrm{CuSO_4} & = 232 \\ \mathrm{Cu} & \mathrm{CuSO_4} & = 40 \end{array}\right\} \begin{array}{l} \text{total electromotive force} = 232 - 40 \\ \quad = 192, \end{array}$$

a value agreeing with that obtained by direct observation. A similar agreement between the sum of the differences of potential and the total electromotive force in the Latimer-Clark's cell is also noticed.

V. H. V.

Property of the Alkalis of increasing the E.M.F. of Zinc. By J. H. KOOSEN (*Ann. Phys. Chem.* [2], **32**, 508—515).—Grove, Joule, Poggendorff, and others have observed the increased E.M.F. obtained by substituting aqueous potash or soda for the dilute acid in a cell. The author states that according to his researches the alkali, say potassium hydroxide, has a four-fold action: (1) it breaks up into potassium and oxygen; (2) potassium replaces zinc in its electrical action, for instance, in a Daniell's cell potassium sulphate is formed in place of zinc sulphate, as the copper is deposited; (3) the zinc is oxidised by the oxygen of the potash; (4) the resulting zinc oxide is dissolved by the aqueous potash. (1) Diminishes the E.M.F., whilst (2) and (3) increase it; (4) may possibly slightly increase it, but it would be desirable to have positive evidence on this point.

If the external resistance of a cell is very great, almost the whole heat of combination will be developed in the external circuit. Let the E.M.F. of a Daniell's cell be taken as the unit of E.M.F., and let the unit of heat be the amount generated in a Daniell's cell by the decomposition of *n* grams of zinc, where *n* is the atomic weight of that metal. Then from Thomsen's determinations, the E.M.F. of a Daniell's cell is given by the equation $ZnSO_4(248) - CuSO_4(198) = 50 = 1$ Daniell; and with potash substituted for dilute sulphuric acid, $K_2SO_4(337) + 2ZnOH_2O(166) - 2KHO(232) - CuSO_4(198) = 73 = 1{\cdot}46$ Daniell. For the author's zinc-bromine-platinum cell, $ZnBr_2(91) = 1{\cdot}82$ Daniell.

The results thus thoretically obtained in the case of these and a few other simple cells considered by the author agree closely with experimental determinations. The heat of combustion of zinc oxide and potassium is not taken into account, as it is certainly not more than 2 per cent. of that due to the decomposition of zinc in a Daniell's cell, and according to Favre and Silbermann it would seem that this chemical action is merely local, and does not contribute to the electrical energy. Practically the author finds that a Daniell's cell with a solution of potassium hydroxide is very satisfactory for giving continuous currents through a high resistance, and sodium hydroxide gives still better results, as sodium sulphate, being more soluble, does not so readily crystallise on the porous cell.

It is very important to prevent interdiffusion of the fluids as far as possible, and for this purpose the author uses a double porous cell, having the intermediate space filled with a solution of potassium and sodium sulphates respectively, with a small admixture of sulphuric acid to diminish the resistance. Cells of this kind have been kept joined up through a resistance of 20 or 30 ohms for weeks together without any perceptible diminution in the E.M.F. The alkaline solution must not be too dilute or the zinc will soon become coated with oxide.

The author states that his zinc-bromine-platinum cell is still better for giving a continuous current through a high resistance. It requires no porous cell, has a high E.M.F., and has been kept in continuous action for months without any change in the E.M.F., in fact until one or other of the elements was completely decomposed. The only precaution necessary is to cover the bromine with a layer of petroleum, which completely prevents all evaporation and smell.

G. W. T.

Electrolytic Formation of Hydrogen Peroxide at the Anode. By M. TRAUBE (*Ber.*, **20**, 3345—3351).—From the results of previous experiments (Abstr., 1885, 1108), it was concluded that hydrogen peroxide is formed by the union of molecular oxygen with hydrogen. Richarz, on the other hand (this vol., p. 11), maintains that that hydrogen peroxide is produced by the oxidation of water.

When 1 per cent. sulphuric acid is electrolysed in presence of alcohol or hydrogen peroxide at the anode, these are rapidly oxidised. In the electrolysis of a 1 per cent. solution of chrome alum, not a trace of ozone is formed, and chromic acid appears at the anode. When lead is used as anode in the electrolysis of 1 per cent. sulphuric acid, it becomes covered with lead peroxide. These experiments point to the presence of free oxygen-atoms which only unite to passive molecules when there is nothing to oxidise, and also show that water is not oxidised by oxygen-atoms. In the electrolysis of sulphuric acid, it is suggested that persulphuric acid is formed by the action of nascent oxygen, and that this decomposes into sulphuric acid (2 mols.) and hydrogen peroxide (1 mol.).

As further proof in favour of the constitution previously ascribed to hydrogen peroxide (Abstr., 1886, 660), it is mentioned that the peroxides of hydrogen, of the alkalis and alkaline earths, of zinc, cadmium, and copper, have quite different chemical properties from those of lead, silver, manganese, and nickel, &c. Only those of the first group yield hydrogen peroxide when treated with acids. The peroxides of the second group can all be prepared by oxidising the oxides or hydroxides in alkaline solution. The peroxides of the first group possess powerful reducing properties, whilst those of the second group are indifferent to oxidising agents. Hence it is concluded that the peroxides of the two groups are differently constituted, and that hydrogen peroxides cannot have the formula HO·OH. The constitution represented by the formula $H\cdot O \vdots O\cdot H$ is considered to be the only one possible. N. H. M.

Electrolytic Conductivity of Halogen-compounds. By W. HAMPE (*Chem. Zeit.*, **11**, 816; 846—847; 904—905; 934—935; 1109—1110; 1158).—Pure dry salts fused in hard glass tubes or porcelain crucibles, or dissolved in dry ether or absolute alcohol, were submitted to a current from eight large Bunsen chromic acid cells, platinum electrodes being used when the conditions of experiment permitted. The following salts proved good electrolytes in a state of fusion:—All the haloïd salts of lithium, sodium, potassium, rubidium, and cæsium, beryllium chloride, magnesium chloride and bromide, strontium and calcium chlorides and bromides (part of the liberated metals combining with the silica of the glass or porcelain), barium chloride, lanthanum, didymium, and cerium chlorides (this confirms Hillebrand and Norton's experience), indium chloride, thallous and cuprous chlorides (thallic and cupric chlorides decompose when fused), tantalum chloride, and thorium chloride, although the latter is not suitable for electrolysis, as the melting and boiling points are near together. In concentrated alcoholic solutions, cupric chloride behaves as an electrolyte. Gold chloride in carbon bisulphide is a non-conductor; when mixed with ether a pasty mass forms, and the supernatant liquid gradually deposits gold; this liquid conducts slightly, and after 15 minutes the negative pole becomes gilded. Aqueous solutions of gold chloride owe their electrolytic conductivity to the presence of hydrochloric acid. Zinc and cadmium iodides, bromides, and chlorides are good electrolytes when fused, but their conductivity ceases on solidification. In concentrated solutions, these salts conduct well, in weak solutions badly; in absolute alcohol all, but only zinc chloride and bromide dissolve in ether and conduct well, whilst the other salts dissolve in ether and conduct only sparingly or not at all. Fused mercuric chloride, bromide, and iodide are feeble electrolytes, especially the first; in solution in ether, none conduct, owing probably to sparing solubility; in absolute alcohol, they conduct slightly; better when the solution is hot than when it is cold. Mercurous chloride fused in closed glass vessels proved electrolytic. Aqueous solutions of mercuric chloride conduct badly at first, with deposition of mercury and mercurous chloride, and evolution of oxygen and chlorine; subsequently mercury only is deposited, and the electrolysis proceeds at a quicker rate; in this case the current in the first instance produces electrolytes (hydrochloric acid for instance), and when these are present in abundance the process goes well.

Fused gallous chloride is a very good conductor, globules of metal separate at the negative pole, but the chlorine at the positive pole combines with the gallous chloride to form gallic chloride; the latter is not such a good conductor as gallous chloride, no metal separates, evidently owing to its entering into combination with the gallic chloride to form gallous chloride. Stannic chloride does not conduct; when electrolysed in aqueous solution the hydrochloric acid only conducts, the tin being set free by the hydrogen (Hittorf has stated the contrary). Fused stannous chloride on the other hand is an excellent electrolytic conductor, the current continues to pass even on cooling as long as the mass remains soft, but ceases to flow when the chloride is solid. Fused lead chloride, bromide, and iodide conduct very well with vigorous decomposition, and, unlike the other salts examined, they conduct when solid; Buff characterised this conduction as metallic, Wiedermann regarded it as electrolytic; the author confirms the latter view. At ordinary temperatures, no current passes through the cold fused lead salts; it is first observed to flow at 110° through the chloride, at 115° through the bromide, and at 150° through the iodide, the conductivity then increases as the temperature rises, in the manner usual with electrolytes. The trihaloïd compounds of antimony in a fused state behave as feeble electrolytes, the tri-iodide being the best; but in carbon bisulphide solutions they do not conduct electricity. Vanadium tetra- and tri-chlorides do not conduct, but when decomposed with water the solutions electrolyse, but in neither case is the metal deposited. The following are non-conductors:—Fused aluminium chloride or bromide (Buff's statement to the contrary is probably based on experiments with impure chloride), boron chloride, titanium and silicon tetrachlorides and bromides, vanadyl chloride, niobium pentachloride, all the haloïd compounds of phosphorus, arsenic trichloride, and antimony pentachloride. Yttrium and zirconium chlorides sublime without melting, and when the former is dissolved in water it conducts on account of the hydrochloric acid, but no metal is deposited; the latter is a non-conductor; titanium hexa- and di-chlorides are infusible solids, so do not come under consideration. D. A. L.

Molecular Heats of Gases. By H. LE CHATELIER (*Bull. Soc. Chim.*, **48**, 122—124).—The fact that the curves of the specific heats of carbonic anhydride and water vapour converge to a point below zero, leads to the supposition that molecular heats of all gases tend to the same limit as the temperature approaches absolute zero. The author has compared the specific heats, calculated on this assumption, with the actual determinations of Wiedemann. The specific heats can be represented by the expression $C = 6{\cdot}8 + \alpha[273 + t]$, α being a constant which depends on the nature of the gas and has a higher value the more complex the molecule. The numbers calculated by this equation differ from the actual numbers by quantities less than the experimental errors. A similar agreement is found between the numbers for carbonic anhydride at high temperatures deduced from this equation and the actual numbers obtained by the author and Mallard. C. H. B.

Influence of Small Amounts of Impurities on the Vapour-tension of Liquids. By G. TAMMAN (*Ann. Phys. Chem.* [2], **32**, 683—699).—The increase in the vapour-tension of a liquid observed by Wüllner and Grotrian (*Ann. Phys. Chem.* [2], **11**, 545), when the space occupied by its vapour in the manometer has been decreased by compression, and attributed by them to a dependence of the tension on the amount of liquid in contact with the vapour, is shown to be caused and brought about by traces of impurity in the liquid. These traces are often so exceedingly small as not to be recognisable by the ordinary tests. But the vapour, if containing this impurity, consists of a mixture of two substances one of which is more volatile than the other, so that compression causing a greater condensation of the less volatile, causes a rise in the vapour-tension, and expansion has just the opposite effect. A difference is therefore observed between the tension measured after compression and after expansion. This difference is reduced in magnitude by purification of the liquid used, but could not in any case be entirely eliminated, although an approximation to a constant tension was reached in the case of water. A measurement of the vapour-tension, once after compression and once after expansion, will give a rough measure of the purity of the substance used. Experiments are given with water, ether, carbon bisulphide, benzene, methyl and ethyl alcohols, chloroform and acetic acid. H. C.

Dissociation of Crystallised Lead Acetate and Sodium Thiosulphate. By W. MÜLLER-ERZBACH (*Ber.*, **20**, 2974—2981).—Two series of experiments were made with lead acetate. In the first series, large crystals of the commercial salt were employed in the state of powder, and with it the relative tension was 0·27 to 0·38 at temperatures varying between 12·5° and 21·8°; whilst in the second series, in which small crystals of the pure salt were used, the relative tension was 0·32 to 0·39 at 14·9—24·3°; the value of $t_1 - t_2$, which the author assumes to be a measure of the attraction between the salt and its water of crystallisation (compare Abstr., 1887, 628), decreasing with the rise of temperature. A partially dehydrated specimen of the salt containing about ½ mol. H_2O, when placed in a moist atmosphere until water equal in amount to 3 mols. had been absorbed, showed a higher and less constant relative tension, the highest value being 0·485 at 21·5°.

With sodium thiosulphate, $Na_2S_2O_3 + 5H_2O$, two series of experiments were also made, and in the first series 3 mols. H_2O were lost with a relative tension = 0·33 to 0·36 at 29·1—32·9°, and a further 1·4 mol. with a relative tension = 0·17 to 0·22 at 31·7—34·2°, the remainder of the water being given off with a relative tension = 0·047 to 0·053 at 50·6—52·7°. The second series of experiments showed that 3 mols. were lost with a relative tension = 0·26 to 0·28 at 18·3—21·6°, that a further 1·4 mol. was lost with a relative tension = 0·08 to 0·12 at 15·9—22·1°, and that the tension became imperceptible when the salt contained 0·6 mol. H_2O. The partially dehydrated salt, containing 2 mols. H_2O, exposed in a moist atmosphere until it contained 4·75 mols. H_2O, lost 2·55 mols. with a relative tension = 0·29 to 0·31 at 23·6—25·9°, and the salt with 2 mols. H_2O, obtained in like manner from the salt + 0·49 mol. H_2O, lost approximately 1·5 mol. with a relative tension = 0·10 to 0·19 at 5·3—16·1°. It was found, however, that when sodium thiosulphate was heated to drive off the water of crystallisation rapidly and then exposed to moist air until 4·9 mols. H_2O had been taken up, it lost the whole of the water with a relative tension = 0·21 to 0·32 at 15·8—30·6. W. P. W.

Relation between the Compressibility of a Solution and the Compressibilities of its Constituent Parts. By F. BRAUN (*Ann. Phys. Chem.* [2], **32**, 504—508).—Röntgen and Schneider (this vol., p. 22) have given for the compressibility of rock-salt the value 5×10^{-6}, which does not agree with the author's previous determination (Abstr., 1887, 436), which gave $1·4 \times 10^{-6}$. This result was obtained by comparatively rough methods, but the author points out that it agrees very closely with the value $1·6 \times 10^{-6}$, deduced from Voigt's determination (*Ann. Phys. Chem. Ergbd.*, **7**, 214) of its two coefficients of elasticity.

Röntgen and Schneider assume that if γ be the compressibility of a solution containing per unit volume a volume V' of water, and V'' of salt, and if γ' be the compressibility of water and γ'' that of the salt, then (1) $\gamma = \gamma'V' + \gamma''V''$. Now if n be the number of molecules in a solution containing a percentage p of salt of molecular weight m, then (2) $n = 10^6p/m(100-p)$. They then take a constant a such that (3) $n = aV''/V'$, and eliminating V' and V'' from equations (1) and (3), they obtain the equation $(\gamma - \gamma')(n + a) = (\gamma' - \gamma'')a$, which they write $(y - b)(n + a) = (1 - b)a$, where y is the apparent compressibility of the solution, and b that of the salt. If κ be the cubic compressibility of glass, (5) $y = (\gamma - \kappa)/(\gamma' - \kappa)$, and

$b = (\gamma'' - \kappa)/(\gamma - \kappa)$. They determined n and y for five different concentrated solutions of sodium chloride. Two of these results they used to determine a and b by means of (4). They then found that by substitution in (4) the relations obtained between n and y agreed well with the experimental determinations. Assuming the formula to hold good when n becomes infinite, y will in that case be equal to b, and determining γ'' from (5), they obtained values varying from $4{\cdot}7 \times 10^{-6}$ to $4{\cdot}8 \times 10^{-6}$, which agreed well with the value 5×10^{-6} determined directly for the solid salt.

In a previous memoir, the author found that (1) does not agree with experiment, if for example γ' were given, γ'' would have to be negative to give the correct value of γ. If, therefore, the compressibility of a solution is equal to the sum of the compressibilities of its constituents, the compressibility of the water of the solution must be diminished by the presence of the salt, and this is shown to be the case by Röntgen and Schneider's recent results. The other discrepancy the author traces to these observers having determined the value of a from two equations of the form (4), the observations then show that a and b are constants, so that if the value of V″ calculated from (3) be substituted in (1), this equation will naturally agree with experiment, since it is merely another form of (4). The value of a can, however, be obtained directly from (2) and (3), and the value thus obtained is about five times as great as before, and (1) will only hold good for this value of a, for then only does the ratio V″/V′ express the actual conditions. With this value of a, b is no longer found to be a constant. The author gives a numerical example, in which Röntgen and Schneider's value of a leads to an impossible result. He observes that as this correction does not alter the form of (4), all conclusions drawn simply from the form of this equation will still hold good. G. W. T.

Dilatation and Compressibility of Liquids. By E. H. AMAGAT (*Compt. rend.*, **105**, 1120—1122).—The author has determined the expansion and compressibility between 0° and 50°, and 1 atmosphere and 3000 atmospheres, of water, of ether, of methyl, ethyl, propyl and allyl alcohols, of ethyl chloride, bromide and iodide, of carbon bisulphide and of phosphorous chloride.

In all cases, except that of water, the coefficient of expansion diminishes with increased pressure, but the rate of diminution decreases as the pressure rises, although it remains distinct even at 3000 atmospheres. The increase in the coefficient of expansion due to a rise of temperature, likewise diminishes under increased pressure. The coefficient of expansion of ether under a pressure of 3000 atmospheres is only one-third of its value at normal pressure, and when this liquid is compared with carbon bisulphide, it is found that whilst under normal pressure the ether is much the more expansible of the two, under 2500 atmospheres the coefficients are identical, and under 3000 atmospheres the coefficient for carbon bisulphide is higher than that for ether.

Under very high pressures, the perturbations which are observed in the case of water, and which are due to the existence of a point of maximum density, gradually disappear, and under 3000 atmospheres the law of expansion of water agrees with that of other liquids (compare Abstr., 1887, 695). C. H. B.

Compressibility of an Aqueous Solution of Ethylamine. By F. Isambert (*Compt. rend.*, **105**, 1173—1175).—The coefficient of compressibility of ethylamine between 5° and 7° and from 8 to 45 atmos. is 0·000120, a value which approximates to that for ether at 0°, and is much higher than that for water. The compressibility of an aqueous solution of ethylamine is much lower than the value calculated on the assumption that the two liquids are simply mixed, and it decreases as the proportion of water increases. Ethylamine in fact behaves like ammonia, and this result confirms the author's conclusion that solutions of the ammoniacal bases behave like true chemical compounds more or less dissociated in presence of excess of water. The view that a compound is formed is supported by the contraction which takes place, and the development of heat, which as in the case of ammonia is equal to the heat of volatilisation of the amine.

C. H. B.

Oxygen Carriers. By L. Meyer (*Ber.*, **20**, 3058—3061).—Experiments were made with various metallic salts with a view to determine their power of expediting the oxidation of sulphurous acid. The oxygen and sulphurous acid were passed, for four hours, at as uniform a rate as possible, through the solution of known concentration contained in a flask heated on a water-bath. The amount of sulphuric acid was then determined.

The most active salt was manganous sulphate, of which 2·404 grams ($MnSO_4 + 5H_2O$) was dissolved in 200 c.c. of water; this solution in four hours gave six times as much sulphuric acid as the salt contained. Manganous chloride is also very active; copper sulphate gives less sulphuric acid. After copper salts, the salts of iron and cobalt are the most active, the chlorides being more so than the sulphates. The salts of nickel, zinc, cadmium, and magnesium produce less sulphuric acid, whilst dilute solutions of thallium and potassium sulphates and free sulphuric acid produce none at all (compare Kessler, *Ann. Phys. Chem.*, 1863, 119, 218). N. H. M.

Explosive Decomposition of Picric Acid and other Nitro-derivatives. By Berthelot (*Compt. rend.*, **105**, 1159—1162).—When picric acid is heated in a capsule, it melts and gives off inflammable vapours, which burn with a smoky flame, but it does not explode. A small quantity when heated in a closed tube can be sublimed without decomposition. If, however, the picric acid is thrown into a vessel previously strongly heated, the quantity of the solid being so small that the temperature is not materially reduced, then it decomposes with detonation accompanied by a vivid flash of light. When the quantity of picric acid introduced is sufficient to somewhat cool the bottom of the vessel, detonation does not take place at once, but the acid is partially volatilised, and a somewhat less violent explosion follows. If the quantity is still larger, the acid decomposes, but there is no explosion. Similar results were obtained with mono- and dinitrobenzene, and mono-, di-, and tri-nitronaphthalene. The tendency to detonate increases with the number of NO_2 groups.

Nitro-derivatives may decompose in several different ways. If the heat developed by combustion is carried away with sufficient rapidity, there is no deflagration or detonation, but if the heat accumulates the temperature may rise sufficiently high to produce detonation. The heating of only a small part of the containing vessel to a high temperature may produce an explosive wave, which may then propagate itself through the whole mass, and thus produce an explosion.

C. H. B.

Relative Size of the Molecules, calculated from the Electric Conductivity of Salt Solutions. By G. JÄGER (*Monatsh.*, 8, 498—507).—In this paper, an attempt is made to determine the relative diameters of some of the elementary molecules and atomic groupings, adopting as a basis for the calculations the results obtained by Kohlrausch in his investigations on the electric conductivity in aqueous solutions of certain metallic hydroxides and salts.

If, in such an aqueous solution, a cylindrical section is taken of unit dimensions, there are contained therein m electrochemical molecules; taking, then, the electromotive force in the direction of the axis as unity, the kathion will be propelled in the one direction with velocity U, and the anion with velocity V in the other. If ϵ is the quantity of positive or negative electricity with which each molecule is endowed, then the coefficient of conductivity $\kappa = (u + v)m$ where $\epsilon U = u$ and $\epsilon V = v$, and the specific molecular conductivity $\lambda = u + v$. But according to Hittorf $v/u + v = n$, in which n is the number of molecules passing in unit time through unit space. Hence $u = (1 - n)\lambda$ and $v = n\lambda$. If the molecules of the ions pass with a certain velocity, they meet in unit time a certain number of other molecules of a different kind passing in the opposite direction; therefore they require a certain amount of energy to overcome the necessary resistance which is proportional to their rate of passage. If for the sake of simplicity the molecules are assumed to be spheres, and the solution is so dilute that there is no interaction between the molecules of the dissolved substance; also if a molecule of radius r passes in a certain direction whilst the environment consists of molecules of radius ρ, and the number of molecules in unit volume is α, then $r + \rho = R$ if the forces are resolved in two directions. The result is the same if the radius of the moving molecule is R, whilst the molecules in the environment are reduced to a mathematical point.

Now (1) $v = C/R^2 = C/(r + \rho)^2$, in which C is a constant obtained by integration, while for another molecule (2) $v' = C/(r' + \rho)^2$; dividing (1) by (2) $v/v' = (r' + \rho)^2/(r + \rho)^2$, from which $r = (r' + \rho)\sqrt{v'/v} - \rho$. To solve this equation the values for the relative velocities have been determined by Kohlrausch, whilst to find r' and ρ the diameters of the molecules of water and chlorine calculated by O. Meyer are used. The values are for water $d = 96 \times 10^{-9}$, for chlorine $\delta = 44 \times 10^{-9}$ centimetres, while U for water = 49. Hence the diameter of a given molecule is—

$$d = \sqrt{\frac{960,400}{v}} - 44$$

expressed in 10^{-9} centimetres. The following results are given for the relative diameters of the elementary molecules and of certain atomic groupings arranged in order of magnitude.

H.	½H_2.	I.	Br.	(CN).	Cl.	K.	(NH_4).	(NO_2).	(ClO_3).
15	32	91	91	95	96	97	99	100	111

½K_2.	½(SO_4).	Ag.	½$(NH_4)_2$.	½(CO_3).	½Ag_2.	Na.	F.	½Ba.
111	111	111	117	119	129	132	135	138

½Cu.	½Sr.	½Ca.	½Mg.	$(C_2H_3O_2)$.	½Na_2.	½SO_4.*	Li.	½Zn.
138	141	148	160	160	165	165	170	175

½Mg.*	½Zn.*	½Cu.*	½Li.*
218	239	239	251

The values marked thus * were determined by the electric conductivity of magnesium, copper, and zinc sulphate.

It will be seen that the relative size of the molecules is most variable, that of lithium, for example, being more than 16 times greater than that of hydrogen, both being expressed in linear dimensions. It is further to be noticed that the diameters of the double molecules of the elements, as for instance hydrogen, is greater than that of twice the single molecule, but this result would be a necessary consequence of the union of two spheres of equal volume.

The elements belonging to the same family in Mendeléeff's scheme, such as chlorine, bromine, iodine, or barium, strontium, and calcium, come close together in the table. If a substance is in the solid or liquid state, the number of molecules in unit volume is directly proportional to the volume of the molecule; multiplying this number by the molecular weight, values should be obtained proportional to the specific gravities of the elements in question, or conversely similar proportional numbers should be obtained by dividing the molecular weight by the molecular volume. However, this relation does not always hold good, except in the case of certain chemically allied elements. Hence it follows that different molecules consist of ultimate particles differently arranged. V. H. V.

Representation of Atoms in Space. By W. Lossen (*Ber.*, **20**, 3306—3310).—If atoms be considered as material points, the tetrahedron employed in the Van't Hoff-Le Bel hypothesis to represent the compound $C(R_1R_2R_3R_4)$ may be replaced by the straight lines joining the points at the solid angles where the radicles are assumed to be situated with a point in the centre representing the carbon-atom. The attractive forces by which the radicles $R_1R_2R_3R_4$ are held by the carbon-atom must then act in the directions of these straight lines, the said directions being solely dependent on the positions of the atoms in space. A combination of two carbon-atoms is then effected by an attraction acting along and represented by the straight line joining them. By such a representation, however, a double union would be in no way distinguishable from a single one, both deing denoted by a straight line joining the carbon-atoms. The author considers this to indicate a weak point in the Van't Hoff - Le Bel hypothesis, and one requiring explanation. He also concludes that a polyvalent atom cannot be represented as a point in space, but that various portions of such an atom having different affinities must be distinguished. H. C.

Inorganic Chemistry.

Preparation of Hydrogen Iodide. By L. MEYER (*Ber.*, **20**, 3381—3383).—100 parts of iodine contained in a retort are moistened with about 10 parts of water. The retort is then fitted with a funnel closed with a glass rod, containing 5 parts of amorphous phosphorus mixed with 10 parts of water. One drop of water containing phosphorus is let into the retort; more phosphorus is slowly added, after which large amounts may be added. The mixing is completed in a quarter of an hour. If more than a drop is added at first, the action cannot be controlled, and will generally result in a violent explosion. No heating is necessary. The iodine carried over by the hydrogen iodide is nearly all deposited in the neck of the retort, which is inclined upwards.

By using 100 grams of iodine, 5 grams of phosphorus, and 25 c.c. of water, 95 grams of hydrogen iodide (of which 37·5 grams were obtained by distillation) were obtained, instead of 100·8 grams. With 20 grams of water 98·1 grams were obtained (74·4 grams as gas and 23·7 grams by distillation). N. H. M.

Products and Rate of Decomposition of the Salts of the Halogen Oxy-acids by Heat. By A. POTILITZIN (*Chem. Centr.*, 1887, 1218, from *J. Russ. Chem. Soc.*, 1887, 339—357).—Between 330° and 400°, barium chlorate decomposes entirely according to the equation $2Ba(ClO_3)_2 = BaCl_2 + Ba(ClO_4)_2 + 4O$. Between 400° and 470°, barium chloride and oxygen are the only products. The rate of the decomposition rises with the temperature up to 400°, whilst if the temperature remains constant, the decomposition rises at first, and then gradually falls again, although it is not complete. According to the author, barium chlorate decomposes to some extent before it melts. Barium perchlorate crystallises with 3 mols. H_2O, whereas Marignac gives the formula $Ba(ClO_4)_2 + 4H_2O$; also, contrary to Marignac's statement, it is not hygroscopic. It loses 2 mols. H_2O by remaining over sulphuric acid, and the third molecule is expelled at 100°.

Barium bromate becomes anhydrous at 170°, the crystals turning slightly yellow, without, however, losing their crystalline form or lustre. Decomposition begins at 260°, and at 300° bromine is evolved. The decomposition becomes complete without the salt melting. The author draws the conclusion that the bromate is changed into two isomeric salts, namely $Br^{v}O_2 \cdot OM$ (the original salt), and $MBr^{vii}O_3$, and that these, therefore, decompose at different rates. He could not find any perbromate in the product of decomposition. J. W. L.

Mutual Displacement of the Halogens in their Compounds with Oxygen. By A. Potilitzin (*Chem. Centr.*, 1887, 1218—1219; from *J. Russ. Chem. Soc.*, 1887, 358—364).—The author believes that these reactions are much more complex than is usually supposed. By the action of chlorine on a solution of sodium bromate in the dark, he obtained a mixture of sodium chloride and bromide, and bromic and chloric acids together with free bromine. He finds that chlorine acts in the same way on potassium bromate and on barium bromate; experiments were also made on the dry salts, when the same products seemed to be formed. Bromine was also found to act on the chlorates in the same way, although much less energetically. These reactions take place much more readily in a sealed tube. Iodine and the iodates were also included in the series of experiments with similar results. J. W. L.

Preparation of Hydrogen Sulphide Free from Arsenic. By C. Winkler (*Zeit. anal. Chem.*, **27**, 26—27).—Barium sulphate (powdered barytes) is mixed with 25 per cent. of ground coal and 20 per cent. of common salt. The damped mixture is rammed into a clay crucible, which after drying and closing with a luted cover is heated for several hours at an incipient white heat. The product is in hard compact masses which dissolve completely in dilute hydrochloric acid with a steady evolution of hydrogen sulphide.

M. J. S.

Selenites. By Boulzoureano (*Bull. Soc. Chim.*, **48**, 209—210).—Solutions of metallic salts were mixed with sodium selenite and the resulting precipitates were heated in sealed tubes at 200° with very dilute selenious acid. Ferric selenite forms small, golden-yellow prisms which separate in radiating groups.

Another method consists in treating a metallic carbonate with dilute selenious acid, mixing the solution with its own volume of water, and heating in sealed tubes at 200°. This was employed for the preparation of the cobalt, nickel, manganese, and cadmium salts.

Cobalt selenite forms transparent, violet prisms, nickel selenite forms large, short, green prisms arranged in radiating groups. If the original solution is mixed with sodium selenite, yellow crystals are obtained. Manganese selenite crystallises in short, pale-red prisms or in slender, brown needles if heated beyond 230°. The cadmium salt forms long, colourless, transparent prisms, or much shorter yellow crystals if heated at about 200°. Zinc seems to form a selenite crystallising in prisms.

The liquid obtained by the second method was allowed to evaporate spontaneously at the ordinary temperature or in a vacuum. Crystals are obtained in the case of cobalt and manganese. The latter yields a pink-coloured crust and the former deep violet crystals.

Cupric carbonate, when treated with a warm solution of selenious acid, yields a blue precipitate of the normal selenite, and if this is heated to boiling, it is converted into green, microscopic prisms. The solution is bluish-green, and on cooling deposits large, green crystals. If the normal selenite is heated in sealed tubes with the carbonate and water, it yields well-defined, greenish-yellow, prismatic crystals. Sodium selenite and zinc sulphate in sealed tubes yield white, transparent crystals. C. H. B.

Preparation of Hydrogen Arsenide. By A. CAVAZZI (*Chem. Centr.*, 1887, 1097, from *Rend. Acc. Bologna*, 1886-87, 85—86).—The action of zinc on an acid solution of arsenious acid produces a gas containing 70 per cent. by volume of hydrogen arsenide. Sodium amalgam containing not more than 4 grams of sodium in 50 c.c. of mercury, by its action on a concentrated solution of arsenious acid, produces a gas containing 86 per cent. by volume of hydrogen arsenide. A gas containing a large quantity of arsenic may be prepared by the action of aluminium on a somewhat dilute alkaline solution of potassium arsenite, whilst a solution of arsenic disulphide in potash, when subjected to the action of aluminium, evolves a gas quite free from arsenic. J. W. L.

Action of Hydrogen Arsenide on Arsenious Acid. By D. TIVOLI (*Chem. Centr.*, 1887, 1097, from *Rend. Acc. Bologna*, 1886–87, 98).—The reactions of hydrogen arsenide on arsenious acid dissolved in hydrochloric and sulphuric acid respectively are expressed by the equations:—$2AsH_3 + 2AsCl_3 = 6HCl + As_4$ and $3(AsO_2)SO_4 + H_2SO_4 + 6AsH_3 = 3As_4 + 4H_2SO_4 + 6H_2O$. The precipitation of the arsenic does not take place in neutral solutions, whereas in the hydrochloric acid solution it is complete, and in the sulphuric acid solution almost so. J. W. L.

Lowest Compounds of Silver. By O. v. D. PFORDTEN (*Ber.*, **20**, 3375—3381; compare Abstr., 1887, 699).—According to Stas, silver is oxidised in the cold in presence of water containing dissolved air and acidified with hydrochloric, sulphuric, or acetic acid, &c. Experiments made by the author show that when a solution containing potassium permanganate and sulphuric acid is boiled in a current of carbonic anhydride it is not capable of dissolving finely divided silver; on admitting air to the solution, silver dissolves and the permanganate becomes decolorised. This accounts for the result previously obtained (*loc. cit.*) when silver was boiled with dilute sulphuric acid and treated with a drop of permanganate solution; the solution being free from air, the permanganate did not decolorise. In presence of air, the reaction is very slow, and in the titration of the argentous oxide with permanganate, none of the silver formed is dissolved (compare Friedheim, Abstr., 1887, 1079).

With regard to Friedheim's supposition (*loc. cit.*) that the argentous oxide is a mixture of silver and argentic oxide or organic matter, it is mentioned that the preparation previously described contained no carbon and dissolved in nitric acid without leaving a residue; when shaken for 12 hours with mercury, it underwent no change in properties or appearance. It is therefore maintained that the substance cannot be metallic silver. The examination of the substance will be continued. N. H. M.

Behaviour of Basic Slag with Water charged with Carbonic Anhydride. By M. A. v. Reis (*Chem. Zeit.*, **11**, 933—934; 981—982).—In these experiments, which are a continuation of those previously made by him (Abstr., 1886, 663), the author has included nine samples of slag from different sources; two samples of precipitated slag; one sample each of di-, tri-, and tetra-calcium phosphate (the last synthetically prepared), also bones, bone-ash, and phosphorite. Ten grams of the finely powdered phosphate supported on a platinum cone covered with asbestos in a funnel, were treated with water saturated with carbonic anhydride percolating at the rate of 1 litre in three hours. One slag was treated with 50 litres of carbonic anhydride solution; each litre of the first 10 litres of percolate was examined separately, but subsequently examinations were made at definite intervals. Silica and phosphoric acid pass through in nearly constant quantities in proportions approximating to their relative amounts in the original slag up to the 25th litre, after which their solubility rapidly decreases; lime, however, continues to dissolve even in the 50th litre. Although the various changes take place simultaneously at first, the free lime is most readily attacked, then the calcium silicate and phosphate, and finally the other compounds of calcium (probably ferrite or manganate). The exhausted slag amounted to 30·07 of the original; its composition (I), and that of the original slag (II), is as follows:—

	SiO_2.	P_2O_5.	CaO.	MgO.	MnO.	FeO.	Fe_2O_3.
I.	2·30	2·25	14·7	6·65	9·09	18·41	35·90
II.	7·67	16·32	47·98	2·47	4·18	8·90	7·41

	Al_2O_3.	Insoluble.	Loss on ignition.
I.	5·52	2·25	3·10
II.	—	0·47	—

The slight solubility of the magnesia is noteworthy. The other phosphates and slags were treated each with 10 litres of carbonic anhydride water, and the percolates were examined in two lots of 5 litres each. Full numerical details are given, from which the following table is taken, showing the relative solubility of the phosphoric acid, silica, and lime in the various phosphates examined; the figures are percentages of the amount of each constituent in the original substances:—

	SiO_2.	P_2O_5.	CaO.
Slags	86·1—27·4	48·1—22·9	57·5—34·4
Tetracalcium phosphate	—	42·1	53·0
Bones	—	28·5	28·9
Precipitated slags	7·7—22·7	22·0—33·0	30·1—58·5
Dicalcium phosphate	—	16·8	16·8
Tricalcium "	—	12·5	13·6
Bone ash	—	5·5	5·9
Phosphorite	—	3·1	3·8

The slags varied considerably amongst themselves owing to their different origin and constitution, but along with the tetracalcium phosphate they proved more soluble than the other forms of phosphate; the comparatively high solubility of bone phosphoric acid is due to the organic matter present. It is interesting to note that in experiments with the tetracalcium phosphate after the removal of any excess of lime in the first 5 litres or so, the phosphoric acid and lime wash out in the molecule ratio $1P_2O_5 : 4CaO$, tending to show that this really is a compound of that composition, for had it been a mixture of lime and triphosphate, the lime would have continued to wash out irregularly. In a similar manner, the existence of tetracalcium phosphate in basic slag is illustrated.

The author concludes that he has now set aside v. Maltzahn's adverse criticism of his previous work, and upset any views as to the comparative insolubility of basic slag phosphates. D. A. L.

Tetrabasic Calcium Phosphate and the Basicity of the Silicate in Basic Cinder. By G. Hilgenstock (*Chem. Centr.*, 1887, 1097—1098, from *Stahl u. Eisen*, 7, 557—560).—The author has succeeded in preparing tetrabasic calcium phosphate by fusing together calcium phosphate or phosphoric acid with lime, using fluorspar as a flux. The author points out further that since calcium triphosphate is reduced by metallic iron when fused, it can only be the tetrabasic phosphate which is contained in the basic slag, and that the difference in crystalline form of this phosphate may be accounted for in somewhat the same way as in the formation of the various modifications of antimonious oxide, valentinite and senarmontite. Observations seem to show that as the flux cools, the rhombic plates are first formed, next the hexagonal needles, and finally the monosymmetrical crystals. In conclusion, the author endeavours to prove that the silica can only be present in the form $CaSiO_3$. J. W. L.

Behaviour with the usual Solvents of the Soluble Phosphoric Acid in Superphosphates, which have remained some time in Bulk. By A. Beyer (*Chem. Centr.*, 1887, 1115, from *Rep. anal. Chem.*, 7, 327—330).—In making a series of determinations to compare Petermann's and Wagner's methods for the estimation of the phosphoric acid soluble in ammonium citrate, the author found that not only was the percentage of phosphoric acid soluble in water reduced by long standing in heaps, but also that soluble in ammonium citrate solution as estimated by Wagner's method. The alteration in the percentage of phosphoric acid as estimated by Petermann's method, was less noticeable. In superphosphates containing but little ferric oxide and alumina, the differences between the results obtained by the two methods were not very great, but even at the end of eight days an appreciable loss of soluble phosphoric acid as determined by Wagner's method was observed, which quantity was not so great where considerable quantities of acid had been employed. Petermann's method does not show so great a change in the soluble character of the phosphoric acid in superphosphates after a time. If the superphosphates contain considerable quantities of ferric oxide and alumina, the results as obtained by the two methods vary almost directly after manufacture, which differences increase the longer the superphosphates are kept. Here also the results obtained with Petermann's method remain almost constant, whilst the percentage as determined by Wagner's method, as also the phosphoric acid soluble in water, decreases.

J. W L.

Cadmium Sulphide and the various Cadmium Pigments of Commerce. By G. Buchner (*Chem. Zeit.*, **11**, 1087—1089; 1107—1109).—The author finds that all the forms of cadmium sulphide have the same percentage composition represented by the formula CdS, but that two modifications exist, one lemon-yellow, the simple CdS, the other a polymeride of it, and of a vermilion colour. The variety of colour in different preparations of cadmium sulphide is due to the mixture of these two modifications in varying proportions, and not to the small quantity of soluble cadmium salt retained by the sulphide during its precipitation, as has been suggested. The yellow variety is readily polymerised into the red variety by dilute acids, alkalis, &c., especially when in the nascent state, hence on precipitating solutions of cadmium salts with hydrogen sulphide, at first the yellow sulphide forms, but, as the liberated acid comes into action, the red sulphide is precipitated, and if the solution is acid beforehand, little or no yellow sulphide is produced. The red variety passes through the yellow stage when dissolved in acids. Sodium sulphide produces the yellow sulphide in dilute solutions of a cadmium salt, a reddish precipitate in strong solutions, and a brick-red one in boiling solutions. Polysulphides of potassium or ammonium precipitate the yellow cadmium sulphide mixed with varying quantities of finely divided sulphur, which can be extracted by carbon bisulphide. It is noteworthy that pure (red or yellow) cadmium sulphide is quite stable in light, whereas this mixture of sulphide and sulphur oxidises rapidly in light (not in darkness), becoming dirty white, especially after it is ground with linseed oil.

Cadmium hydroxide also assumes two forms: the simple one prepared by adding sodium hydroxide to solutions of cadmium salts gives rise to the yellow sulphide with sodium sulphide, &c.; the polymeric one is formed when cadmium solutions are poured into solutions of sodium hydroxide or when they are precipitated hot; this hydroxide produces the red sulphide, with an intermediate dicadmium sulphhydroxide, $Cd_2S(OH)_2$, of a fine red colour, but too unstable for a pigment; the author considers this association of red colour with the two cadmium atoms in a single molecule, supports his view of the polymeric character of the red sulphide. When heated carefully, the yellow and red sulphides undergo a series of changes of colour through which they pass on cooling in the reverse order, both returning to yellow, the red sulphide having suffered molecular disarrangement during the heating. When heated out of direct contact with the air they neither sublime nor oxidise beyond just the surface. The author finally goes into the question of cadmium pigments, finds zinc compounds the most ordinary adulterants, and gives various tests by which a good pigment for oil painting may be recognised.

D. A. L.

Action of Water on Lead. By M. Müller (*J. pr. Chem.* [2], **36**, 317—340).—A sample of water from the Ocker was distilled. The amounts of dissolved gases and of ammonia were determined in the first, middle, and last fractions, and the behaviour of the different fractions with lead observed. The water before distillation contained 0·00015 per cent. of ammonia.

	First fraction.	Middle fraction.	Last fraction.
Ammonia	0·00115 p. c.	0·0001 p. c.	0·00008 p. c.
Dissolved gases reduced to 0° and 760 mm. pressure.			
Total volume	2·04 vol. p. c.	1·196 vol. p. c.	0·77 vol. p. c.
Carbonic anhydride	1·159 „	0·178 „	0·025 „
Oxygen	0·269 „	0·316 „	0·232 „
Nitrogen (diff.)	0·612 „	0·702 „	0·513 „

The first fraction scarcely attacked polished strips of pure lead, which became slowly covered with a thin deposit. The water remained perfectly clear. The middle and last fractions acted very energetically, the lead was rapidly corroded, and the water became turbid. In order to ascertain whether the protecting influence of the first fraction was due to the ammonia or the carbonic anhydride it contained, well water, perfectly free from ammonia, was distilled, and the amount of gas dissolved in different portions of the distillate was ascertained.

	First fraction.	Middle fraction.	Last fraction.
Dissolved gases reduced to 0° and 760 mm. pressure.			
Total volume	2·661 vol. p. c.	1·312 vol. p. c.	1·047 vol. p. c.
Carbonic anhydride	2·030 „	0·218 „	0·069 „
Oxygen	0·198 „	0·358 „	0·341 „
Nitrogen (diff.)	0·433 „	0·738 „	0·637 „

In this case also the first fraction showed scarcely any action on lead, after remaining in contact with it for 24 hours. The middle and last fractions attacked it with considerable energy. The protecting influence of the first fractions must be considered as due to their containing a relatively large quantity of carbonic anhydride. Distilled water, which was vigorously boiled for some time and quickly cooled in contact with air, was found to contain 0·04 per cent. of its volume of carbonic anhydride, 0·236 per cent. of its volume of oxygen, and 0·514 per cent. of its volume of nitrogen. The rapid absorption of these gases explains the behaviour of water so treated towards lead. Distilled water, quite free from carbonic anhydride but containing oxygen, scarcely acts on lead, but on exposure to the air the liquid becomes cloudy, owing to the formation of a white precipitate.

Samples of water containing different amounts of carbonic anhydride, but an invariable quantity of oxygen, behave very differently with lead. In one case, when the oxygen present was 0·35 per cent. of the volume of the liquid, and a saturated solution of carbonic anhydride was added until the water contained 0·14 per cent. of its volume, the lead was appreciably attacked. On increasing the carbonic anhydride to 0·6 vol. per cent., the attack became remarkably energetic. With 1 vol. per cent. the action was considerably weaker, and when the carbonic anhydride was increased to 1·5 vol. per cent. the lead was no longer visibly corroded. Water containing 2, 2·5, and 3 vols. per cent. of carbonic anhydride was equally inactive. Water containing carbonic anhydride but no oxygen is practically without action on lead, when atmospheric air is excluded. When strips of lead are immersed for eight days in pure distilled water, recently boiled and cooled out of contact with the air, they do not become tarnished. Before filtration, however, but not after, the water gives a considerable reaction with hydrogen sulphide. Pure water evidently attacks lead with formation of an oxide. Ordinary distilled water in which strips of lead were placed, and from which the air was excluded, contained a maximum quantity of lead at the end of three days, after which the lead was by degrees thrown out of solution. This is explained by supposing that water containing carbonic anhydride and oxygen in contact with lead forms lead carbonate, which dissolves in the excess of the gas; but as more lead oxide is formed, this carbonic anhydride is absorbed, and all the lead falls out of solution as lead carbonate. Distilled water, free from carbonic anhydride, to which minute quantities of ammonia have been added, attacks lead, but is without action on it if carbonic anhydride is present.

Lime water, through which a current of air, perfectly free from carbonic anhydride, was passed, at first slowly dissolved lead, but this was soon again thrown out of solution in the form of minute crystals. The solution attained a maximum after 13 hours, and then decreased. Sodium hydroxide solution behaved in a similar way. In the absence of oxygen, neither lime-water nor sodium hydroxide solution attacked lead. Lead tubing, buried in mortar, and kept in a dry room for a year suffered no change, but when the mortar was occasionally moistened with pure water, corrosion rapidly took place. When soapy water or an alkaline solution of lime was used instead of pure water, the decomposition-products consisted to some extent of red lead.

Ordinary distilled water, to which a small quantity of sodium carbonate was added, dissolved no lead, but the metal became slowly covered with a white, compact coating. When the water contained oxygen but no carbonic anhydride, lead was found in solution after a few hours. A trace of sodium hydrogen carbonate added to distilled water completely prevented the dissolution of lead, and the metal became covered with a protecting crust. Waters containing lead in solution were found to be freed from it by adding sodium carbonate. Pure lead carbonate is soluble in water containing carbonic anhydride; it is reprecipitated by boiling the solution or by adding hydrogen sodium carbonate to it. Evidently lead forms an acid carbonate, which is soluble in water but possesses little stability. Hydrogen calcium carbonate acts in precisely the same way as hydrogen sodium carbonate.

Polished strips of lead immersed in a saturated solution of pure calcium sulphate, containing oxygen, become covered with a hard white coating, but no lead goes into solution. In the absence of oxygen, the metal remains perfectly bright. On placing lead covered with the white crust formed by long immersion in a solution of calcic sulphate, in pure distilled water, no lead went into solution except when a considerable quantity of carbonic anhydride was present. When a trace of hydrogen calcium carbonate was added to the solution, in no case was any lead dissolved. The coating is in all probability a basic sulphate of lead.

The presence of minute quantities of chlorides, nitrates, organic matter, and ammonia in water, did not influence its behaviour towards lead. This seems to depend on the presence of oxygen and carbonic anhydride. Water containing much organic matter, and rich in carbonic anhydride, rapidly corrodes lead, but polished surfaces of the metal remain perfectly bright when immersed in pure solutions of organic compounds, such as starch and sugar, provided no carbonic anhydride is present. G. T. M.

Colloidal Copper Sulphide. By W. SPRING and G. DE BOECK (*Bull. Soc. Chim.*, 48, 165—170).—An aqueous solution of copper sulphide can be obtained by precipitating any copper salt by hydrogen sulphide and washing by decantation with dilute sulphuric acid. As the impurities are removed, the copper sulphide becomes soluble and forms a dark-coloured solution with a slight greenish fluorescence. A purer product is obtained by precipitating with ammonium sulphide. The solution contains hydrogen sulphide and may possibly contain copper hydrosulphide. The former may be expelled by a short ebullition without any notable precipitation of copper taking place. Analysis of the liquid shows that the copper and sulphur are in the ratio required by the formula CuS, and hence the solution contains no copper hydrosulphide. Examination with the spectroscope shows that the solution is a true solution and not simply a turbid liquid. It absorbs half the red, the violet, and half the blue in the spectrum of a lamp flame.

The copper sulphide is precipitated from this solution by the addition of various salts, a list of which is given in the paper, but the power of precipitation bears no simple relation to the molecular weight or molecular volume of the salt. The valency of the metal, however, exerts considerable influence. Alum, chrome alum, and aluminium sulphate, precipitate it when added in very small quantities, and the precipitating power of salts of dyad metals is about 10 times as great as that of salts of sodium and potassium.

Schulze has made similar observations in the case of antimony sulphide, but the copper sulphide is more readily precipitated than the antimony compound. C. H. B.

Stability of Mercuric Chloride Solutions. By V. MEYER (*Ber.*, **20**, 2970—2974; comp. Abstr., 1887, 774).—Further experiments have shown that the solutions of mercuric chloride in the hard Göttingen water, even when preserved in hermetically sealed flasks with or without the addition of common salt, gradually deposit mercuric oxychloride, but less rapidly than when kept in vessels exposed to the air; atmospheric dust, however, does not seem to influence the rate of decomposition in any very marked way. If the solution of mercuric chloride in ordinary water, instead of being exposed to diffused daylight, is kept in the dark in well-stoppered flasks, it is found that practically no decomposition occurs, even after two months in solutions made with Göttingen water, pond water, and a well water charged with organic impurity, to which no addition of salt has been made; the very small amount of decomposition which actually occurs being attributed to the unavoidable exposure to diffused daylight during the repeated examination of the solutions.

W. P. W.

Action of Alumina and Kaolin on Calcium Chloride. By A. GORGEU (*Bull. Soc. Chim.*, **48**, 51—52).—Calcium chloride mixed with alumina, kaolin, or ordinary clay, and fused at a cherry-red heat in presence of moist air, yields crystalline products soluble in dilute acids. With alumina, the crystals are distinct, colourless, mono-refractive, modified tetrahedra. They are anhydrous at 120°, have the composition $6Al_2O_3,10CaO,CaCl_2$, and are slowly decomposed by boiling water. Kaolin alone, or mixed with silica, seems to produce various crystalline compounds, including mono-refractive crystals resembling calcium garnet, but these could not be isolated. After prolonged fusion, the product was treated with dilute hydrochloric acid and a solution of sugar. In this way modified tetrahedra of the composition $3SiO_2,3Al_2O_3,16CaO,2CaCl_2$. were obtained. It would seem that calcium garnet is first formed, and afterwards converted into the chlorosilicate. Calcium garnet, in fact, when fused with calcium chloride and oxide, yields modified tetrahedra similar to those just described. C. H. B.

Soluble Manganese Oxide. By W. SPRING and G. DE BOECK (*Bull. Soc. Chim.*, **48**, 170—172).—This manganese oxide is obtained by acting on potassium permanganate with sodium thiosulphate, and thoroughly washing the precipitate with water. As soon as all the potassium has been removed, a brown solution is obtained, from which the oxide is precipitated on the addition of any salt (comp. Gorgeu, *Ann. Chim. Phys.* [3], **63**, 155). Analysis of the product obtained by evaporation of the brown solution shows that it has the composition $4(MnO_2,H_2O),Mn_3O_4$.

The portion of the original precipitate which is insoluble in water has the composition $Mn_8O_{13},4H_2O$, or $3MnO_2$, Mn_3O_4, Mn_2O_3, $4H_2O$.

The colloïdal manganese oxide is precipitated by salts more readily than colloïdal copper sulphide, and the valency of the metals in the salts has the same influence in both cases. The manganese solution can be kept for a long time in sealed tubes, but if filtered through paper the manganese is completely precipitated. C. H. B.

Potassium Manganite. By A. JOLLES (*Chem. Zeit.*, **11**, 1394—1395).—In a previous communication, it is stated that the following equation: $K_2MnO_4 + C_2H_6O = K_2MnO_3 + C_2H_4O + H_2O$, represents the oxidation which takes place in the author's test for certain impurities in chloroform (Abstr., 1887, 866). This statement has been contested. It is now shown that both aldehyde and the manganite K_2MnO_3 are produced, but in excess of alcohol the latter soon decomposes; when, however, the substances are taken in equivalent quantities, the manganite can be separated and dried over sulphuric acid. It is a yellowish-brown substance; is decomposed by dilute nitric and sulphuric acids, yielding manganese dioxide and hydrated dioxide and potassium nitrate or sulphate. It oxidises sulphurous acid to sulphuric acid, which in the nascent state forms manganese sulphate. Boiled with oxalic or tartaric acid, the manganite dissolves with evolution of carbonic anhydride. On exposure to a current of superheated steam and air, it is partially converted into manganate (compare Rousseau, Abstr., 1887, 552, 892). D. A. L.

Manganese Compounds. By B. FRANKE (*J. pr. Chem.* [2], **36**, 451—468; compare Abstr., 1887, 893, 1016).—By heating 8 grams of potassium permanganate with 100 c.c. of strong sulphuric acid at 100°, and allowing it to cool, a brown crystalline salt, $Mn_2O_3,4SO_3,5H_2O$, is formed. When this is treated with water, it is decomposed into equimolecular quantities of manganous sulphate and the hydrated oxide H_2MnO_3; the salt is probably $Mn_2(SO_4)_3,H_2SO_4 + 4H_2O$.

Manganic sulphate, $Mn_2(SO_4)_3$, is obtained when the above salt is heated more strongly with sulphuric acid, in green crystals, decomposed by water in the same way as the acid salt, showing that the atoms of manganese are of different valency. The salt may therefore be regarded as the manganous salt of an acid, $Mn^{iv}SO_4(O{\cdot}SO_2{\cdot}OH)_2$, analogous to the manganous manganese chloride (Abstr., 1887, 893). $Mn_2(SO_4)_3,K_2SO_4$, is obtained in red-brown crystals by carefully heating 8 grams of potassium permanganate with the mother-liquor from the above acid salt; water decomposes it in a manner similar to the other salts.

Steel-grey, metallic-looking crystals of $H_2Mn_2O_4$ are obtained when either of the foregoing compounds is thrown into very weak aqueous soda; sulphuric acid decomposes it into manganous sulphate and manganous acid, $MnO(OH)_2$, which is thus obtained pure as a brown powder; this points to the formula $Mn{<}\substack{O\\O}{>}Mn(OH)_2$.

The brown colour of the solution of manganese dioxide in strong hydrochloric acid is caused by the presence of manganous acid.

A. G. B.

Permanganates. By T. Klobb (*Bull. Soc. Chim.*, **48**, 240—244).—The author has previously prepared certain permanganates by adding potassium permanganate to ammoniacal solutions of certain metallic salts (Abstr., 1886, 983). He has now obtained similar derivatives from luteocobalt chloride in a similar way.

Luteocobaltic permanganate, $Co_2(MnO_4)_6,12NH_3$, is obtained by mixing warm concentrated solutions of luteocobalt chloride (1 mol.) and potassium permanganate (12 mols.) It separates in the form of a precipitate mixed with a salt which crystallises in hexagonal plates, and is formed in greater proportion when the permanganate is not in excess. The latter can be removed by treatment with cold water, and the luteocobaltic permanganate is recrystallised from water at 60°. It then forms very brilliant, black tetahedra, only slightly soluble in cold water, but more soluble in hot water with partial decomposition. When heated, it detonates, and it also explodes when struck. With hydrochloric acid, it yields manganous chloride and luteocobaltic chloride.

Luteocobaltic chloropermanganate, $(Co_2,12NH_3)Cl_4,2MnO_4$, is prepared by mixing a solution of luteocobaltic chloride (8 mols.) with a solution of luteocobaltic permanganate (1 mol.), filtering rapidly, and allowing to cool. It separates in small, black lamellæ with the form of a regular hexagon, red or brown by transmitted light. It is very unstable, and is decomposed by water with removal of the chloride, but dissolves without decomposition in a solution of luteocobaltic chloride. When heated rapidly, it detonates, but it does not explode on percussion.

Luteocobaltic bromopermanganate is analogous to the chloropermanganate, and is prepared in a similar way, or more simply, by mixing warm solutions of potassium permanganate (3 mols.) and luteocobaltic bromide (1 mol.), and allowing them to remain. It forms brilliant, hexagonal lamellæ, which are much more stable than the chlorine-derivative, and are not decomposed by boiling water.

The salt which is obtained in the preparation of luteocobaltic permanganate, and which crystallises in hexagonal lamellæ, is also obtained by mixing cold concentrated solutions of luteocobaltic chloride (1 mol.) and potassium permanganate (3 mols.), when it separates slowly in violet hexagonal lamellæ of the composition $(Co_2,12NH_3)Cl_2,2KCl,4MnO_4$, very soluble in water with partial decomposition into its constituents. When heated, it behaves like the preceding salts. It may be regarded as a compound of luteocobaltic permanganate and luteocobaltic chloride with potassium chloride. It can also be formed by dissolving luteocobaltic chloropermanganate in potassium chloride solution, or by the action of luteocobaltic permanganate on a large excess of potassium chloride. C. H. B.

Electrolytic Extraction of Antimony. By W. Borchers (*Chem. Zeit.*, **11**, 1021—1022).—The author has based a process for the extraction of antimony (from all its combinations soluble in sodium sulphide solution) on the electrolytic method of Classen and Ludwig (Abstr., 1885, 932) for the estimation of that metal.

The ore is extracted with sodium sulphide solution, using 3 mols. Na_2S for every mol. Sb_2S_3. The concentrated extract is mixed with 3 per cent. of sodium chloride to increase its conductivity, and electrolysed. According to the intensity of the current, the metal is deposited as a powder or in shining scales. To prevent deposition of sulphur, the relation of 1 atom of available Na for every atom of oxidisable sulphur must be maintained, but as the mixture $Sb_2S_3 + Na_2S + 2NaHO$ is too unstable, the above proportions are used; too much sodium sulphide is to be avoided as it increases the resistance of the liquid.

The common salt is easily crystallised from the electrolysed solutions, and the sulphur recovered as sodium thiosulphate without much difficulty. D. A. L.

Antimoniates. By G. v. KNORRE and P. OLSCHEWSKY (*Ber.*, **20**, 3043—3052).—Attempts were made to prepare Fremy's potassium antimoniate, $K_4Sb_2O_7$ (*J. pr. Chem.*, **45**, 209), but without success; it is concluded that that salt does not exist, and that Fremy's compound is a mixture of potassium antimoniate and potash.

Potassium antimoniate, $K_2Sb_2O_6$, contains 5 mols. H_2O when air-dried, and is a white granular salt. 100 parts of water at 20° dissolve 2·81 parts of anhydrous salt. Sp. gr. of saturated solution at 18° = 1·0263. A table is given showing the loss of weight it undergoes at various temperatures; at 330° it contains rather more than 1 mol. H_2O, and the author assumes that 1 mol. H_2O is chemically combined, and that the formula of the air-dry salt is $K_2H_2Sb_2O_7 + 4H_2O$. When the hot aqueous solution is evaporated, a gummy salt remains; when this is dried at 100°, it has the composition expressed by the formula $K_2Sb_2O_6 + 3H_2O$.

Potassium antimoniate was also prepared by the methods of Brunner (*Dingl. polyt. J.*, **159**, 356) and Reynoso (*Annalen*, **80**, 272); details of preparation and results are given (compare Abstr., 1885, 1184). N. H. M.

Mineralogical Chemistry.

Arksutite from Ivigtut in Greenland. By A. E. NORDENSKIÖLD (*Zeit. Kryst. Min.*, **13**, 400—401, from *Geol. Fören. Förhandl.*, **8**, 172—175).—A specimen of arksutite was separated according to Thoulet's method, and gave three different substances: an optically isotropic mineral having a sp. gr. of 3·12 (fluorspar); a mineral lighter than 2·99 (possibly thomsenolite); and a birefractive substance of sp. gr. = 2·994, and giving on analysis the following results:—

Al.	Ca.	Mg.	Na.	F.	Total.
17·28	0·22	0·05	24·72	57·16	99·43

corresponding with the formula $5NaF + 3Al_2F_3$. The composition of arksutite is thus perfectly in accord with that of the chiolite of Brandl. From the optical properties of the two minerals, there can be no doubt that they are identical. B. H. B.

Mineralogical Notes. By G. FLINK (*Zeit. Kryst. Min.*, 13, 401—408, from *Bihang till K. Sv. vet. akad. handl.*, 12, Afd. 2).—The author gives the results of a crystallographical and chemical investigation of the following minerals:—1. Cobalt-glance from Nordmarken; 2. Cosalite from Nordmarken; 3. Pyrochroite from Nordmarken; 4. Magnetite from Nordmarken; 5. Manganomagnetite from Långban; 6. Berzeliite from the same locality; 7. Monimolite from Pajsberg; 8. Xenotime from Hitterö, Norway; 9. Apatite from Nordmarken; 10. Liëvrite from Thyrill, Iceland; 11. Epidote from Nordmarken (28 new planes); 12. Epidote from Mörkhult; 13. Manganese-vesuvian from Pajsberg; 14. Orthoclase from the kraflite of Krafla, Iceland; 15. Titanite from the Fredriksberg Mine, Nordmarken.

The author also describes a new mineral, *harstigite*, from Pajsberg, named after the mine in which it was discovered. The mineral belongs to the rhombic system, and exhibits the forms ∞P, $\infty \breve{P} \infty$, $\breve{P} \infty$, $\infty \breve{P} 2$, $\infty \bar{P} \infty$, $\breve{P} 2$. $a : b : c = 0{\cdot}7141 : 1 : 1{\cdot}01495$. No cleavage was observed. The mineral is colourless, and has a vitreous lustre. Analysis gave the following results:—

SiO_2.	Al_2O_3.	CaO.	MnO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
38·94	10·61	29·23	12·81	3·27	0·35	0·71	3·97	99·89

B. H. B.

Manganese and Uranium Oxides. By C. RAMMELSBERG (*Zeit. Kryst. Min.*, 13, 418—419, from *Ber. Akad. Ber.*, 1885, 97).—The author finds that both artificial Mn_3O_4 and crystallised hausmannite, when boiled with concentrated nitric acid, or treated with dilute sulphuric acid, split up into 2MnO, which dissolves, and insoluble MnO_2. Crystallised manganite is not decomposed by sulphuric acid in the same way. Powdered braunite undergoes decomposition, although not completely. Hausmannite should therefore be regarded as having the composition $2MnO,MnO_2$, whilst the formula of braunite is $MnO,(Mn,Si)O_3$.

The author gives the following new analysis of pitchblende from Joachimsthal:—

UO_3.	UO_2.	PbO.	FeO.	CaO.	SiO_2.	Total.
42·87	40·50	3·25	3·78	3·00	6·60	100·00

The general formula of pitchblende is

$$RO,RO_2 = (UO_2,Pb,Fe,Ca)O,(U,Si)O_2;$$

the formula of the varieties containing thorium is

$$(UO_2,Pb,Fe,Ca)O,(U,Th)O_2.$$

The oxides, Y_2O_3, Er_2O_3, Ce_2O_3, which occur in several varieties of pitchblende, appear to be isomorphically mixed with the compound

RO,RO_2. The latter is thus analogous in constitution to braunite, which crystallises in a similar manner. B. H. B.

Minerals from Carinthia. By A. BRUNLECHNER (*Zeit. Kryst. Min.*, **13**, 391—392, from *Jahrb. nat. hist. Landesmuseums in Kärnthen*, **17**, 1—5).—Among the Carinthian minerals described by the author are the following:—Greenockite from Raibl, as a lemon-yellow coating on slate; garnet from Lamprechtsberg in the Lavanthal, as orange crystals enclosing copper pyrites; tourmaline from the same locality, in short, dark-brown crystals; zoisite from Stanziwurdikopf, green in columnar crystals in mica schist. Analyses are given of two specimens of siderite: I. Translucent crystals, with plane faces, from Wölch; II. Yellowish-white crystals, with curved faces, from Lölling:—

	$FeCO_3$.	$MnCO_3$.	$MgCO_3$.	$CaCO_3$.	Impurities.	Total.
I.	95·10	2·11	2·19	trace	0·59	99·99
II.	94·97	trace	3·22	1·78	0·25	100·22

In addition to other factors, the proportion of calcium, even in small quantities, appears to influence the crystal form of iron carbonate. B. H. B.

Martinite from the West Indies. By J. H. KLOOS (*Jahrb. f. Min.*, 1888, i, Ref., 41, from *Sammlg. geol. Reichsmuseums, Leiden*).—Martinite is a new calcium phosphate pseudomorphous after gypsum, from the phosphorite beds of the Island of Curaçao. The pseudomorphs occur in lenticular crystals, having the form of gypsum $(-P, -\bar{P}\infty, \infty\grave{P}\infty)$. The crystals are colourless and transparent. Their sp. gr. is 2·892 to 2·896. Analysis gave the following results:—

P_2O_5.	CaO.	Loss on ignition.	Total.
47·87	47·63	5·46	100·96

Fluorine is absent. The results of the analysis are in accord with the empirical formula $10CaO,4P_2O_5,3H_2O$. B. H. B.

Diadochite from Visé. By G. CESÀRO (*Zeit. Kryst. Min.*, **13**, 421—422, from *Ann. soc. géol. Belg.*, **12**, 173).—The mineral from Visé, to which the name *destinézite* has been assigned, appears to be a variety of diadochite. An almost white and very pure specimen gave on analysis the following results:—

Fe_2O_3.	P_2O_5.	SO_3.	H_2O.	Hygroscopic H_2O.	C.	Total.
37·60	16·76	18·85	25·35	0·30	1·40	100·26

The mineral on microscopic examination was found to belong to the monoclinic system. B. H. B.

Mineral from Krems in Austria. By E. DRASCHE (*Jahrb. f. Min.*, 1888, i, Ref., 29—30, from *Verh. geol. Reichsanst.*, **19**, 81).—The author gives an analysis of a mineral, erroneously supposed to be bauxite, which is found in considerable quantities interbedded in crystalline schists. The mineral is of a white to yellowish-brown colour. For the analysis, pure white specimens were selected. The results were as follows :—

SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	SO_3.	P_2O_5.	H_2O at 100°.
1·30	38·00	0·75	3·75	4·54	38·85	0·88	0·45

The remainder consists of water and organic substance.

B. H. B.

Manganotantalite from the Ural. By A. ARZRUNI (*Jahrb. f. Min.*, 1888, i, Ref., 18, from *Trans. Imp. Russ. Min. Soc.*).—The crystal described was found in the Bakakin gold washings in the Sanarka district, in the south of the Ural. It exhibits the planes $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $0P$, $\frac{1}{2}\breve{P}\infty$, $\frac{1}{4}\breve{P}\infty$, $\bar{P}2$, $\frac{1}{2}\bar{P}2$. It is semi-metallic and nearly black. In very thin layers the colour is orange to ruby-red. Sp. gr. = 7·37. Analyses gave the following results :—

Ta_2O_5.	Nb_2O_5.	$SnO_2 + WO_3$.	FeO.	MnO.	CaO.	Ignition.	Total.
79·81	4·47	0·67	1·17	13·88	0·17	0·16	100·33

These results correspond with the formula $11MnTaO_6 + FeNbO_6$. This mineral, of which as yet only one crystal has been found, is the member of the tantalite group richest in manganese and tantalum.

B. H. B.

Kainosite, a new Mineral from Hitterö, in Norway. By A. E. NORDENSKIÖLD (*Zeit. Kryst. Min.*, **13**, 399—400, from *Geol. Fören. Förhandl.*, **8**, 143—146).—In consequence of the unusual composition of this new mineral, the author has termed it kainosite from καινός (strange). It consists of a calcium yttrium silicate, mixed with a carbonate and water. The only specimen found is a portion of a hexagonal prism. The optical examination, however, shows that it belongs, not to the hexagonal, but to the rhombic or to the monoclinic system. The mineral is semi-transparent, yellowish-brown, and birefractive. Its hardness is 5·5, and sp. gr. 3·413. Analysis gave the following results :—

SiO_2.	$Y_2O_3 + Er_2O_3$.	CaO.	MgO.	FeO.	Na_2O.	CO_2.	H_2O.	Total.
34·63	37·67	15·95	0·03	0·26	0·40	5·90	5·26	100·10

corresponding with the formula $4SiO_2,CO_2,Y_2O_3(Er_2O_3),2CaO,2H_2O$.

B. H. B.

Chemical Nature of Eudialite. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1887, ii, Ref., 449—451, from *Sitzber. K. Preuss. Akad. Wiss.*, **24**, 441—461).—The author has analysed specimens of this rare silico-zirconate from the principal localities at which it is found. The results of his analyses were as follows :—

	Cl.	SiO_2.	ZrO.	Ce_2O_3.	FeO.	MnO.	CaO.
I.	1·53	49·84	14·01	2·35	5·96	0·64	10·77
II.	1·57	48·88	15·17	4·07	7·28	0·52	10·63
III.	1·70	46·68	15·43	—	7·32	2·82	11·76
IV.	1·44	46·84	16·09	5·19	5·92	1·50	10·52

	Na_2O.	K_2O.	H_2O.	Sp. gr.
I.	13·32	0·75	1·24	2·928
II.	8·80	1·24	2·50	2·908
III.	11·24	0·42	0·90	3·081
IV.	10·70	0·50	1·77	3·000

I. Eudialite from Kangerdluarsuk, Greenland; II. From Brevig, Norway; III. From Sigterö, Norway; IV. From Arö, Norway. The formula given by the author for the eudialite of Greenland and of Brevig is $NaCl,2R'_6R''_3(Si,Zr)_{10}O_{26}$, and for the eudialite of Sigterö and Arö is $NaCl,R'_{12}R''_9(Si,Zr)_{25}O_{65}$. B. H. B.

Zeolites from Chili. By L. DARAPSKY (*Jahrb. f. Min.*, 1888, i, Mem., 65—67).—The author has subjected various zeolites, from the mineralogical collection of the National Museum of Santiago, to chemical examination. The analytical results were as follows:—

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	K_2O.	Fe_2O_3.	Total.
I.	52·67	19·80	11·25	—	16·29	—	—	100·01
II.	54·60	—	29·52	1·06	15·03	—	—	100·21
III.	47·69	25·45	14·05	—	13·25	—	—	100·44
IV.	46·74	25·99	9·11	5·23	12·41	—	—	99·48
V.	45·15	26·53	11·86	2·24	13·81	0·45	—	100·04
VI.	43·57	24·27	21·74	0·96	5·28	—	4·44	100·26

I. Hypostilbite from altered amygdaloïdal porphyry at the Hacienda La Quinta at Curicó; formula, $2CaO,2Al_2O_3,9SiO_2,9H_2O$. II. Okenite from the Rio Putagan; formula, $2CaO,3SiO_2,3H_2O$. This appears to be identical with the zeolite from Greenland termed bordite by Dufrénoy. III. Scolezite, accompanying the okenite; sp. gr. 2·15; formula, $CaO,Al_2O_3,3SiO_2,3H_2O$. IV. Typical mesolite from the Desert of Atacama. V. A dense form of the same mineral coating the weathered rock of the Rodaito Mines in the Province of Coquimbo. VI. Prehnite, in green globular masses, from the Rodaito Mines, associated with calcite crystals, and containing small, black scales or wires of natural amalgam ($Ag_{36}Hg$). B. H. B.

Manganese-bearing Idocrase from Sweden. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1887, ii, Ref., 453, from *Bull. soc. franç. min.*, 9, 22—24).—The mineral occurs with manganese-garnet, manganese-epidote, and manganese-silicate in limestone at the Jakobsberg manganese mine in Wermland. The crystals exhibit the forms 0P, ∞P, ∞P∞, P. In thick plates, the colour is black; in powder, dark-violet. In thin sections, the mineral is highly pleochroic, having an amethyst and orange colour. In chemical composition it is characterised by a remarkably high percentage of manganese, copper, and lead, as is shown by the following analytical results:—

SiO_2.	Al_2O_3.	FeO.	MnO.	CuO.	PbO.	CaO.	MgO.	Total.
38·07	15·88	5·08	4·72	2·16	1·80	25·60	5·07	98·38

B. H. B.

Beryl from Madagascar. By A. Damour (*Jahrb. f. Min.*, 1888, i, Ref., 9, from *Bull. soc. franç. min.*, **9**, 153—154).—The crystal described was found with tourmaline, quartz, and triphane at Farafatrana, on the east coast of Madagascar. It is characterised by its pink colour. Its composition is as follows:—

SiO_2.	Al_2O_3.	BeO.	FeO.	MnO.	CaO.	Ignition.	Total.	Sp. gr.
66·56	18·66	12·47	0·09	0·21	0·06	2·30	100·35	2·72

B. H. B.

So-called Soda Granites. By A. Gerhard (*Jahrb. f. Min.*, 1887, ii, Mem., 267—275).—Although in the analyses of most granites, the percentage of potash exceeds that of soda, yet certain granites are known in which the opposite is the case. Attention was first drawn to such granites in 1856 by Haughton, who termed them *soda-granites*. The author has made a series of careful analyses of typical examples of these rocks, and finds that in the granites of Baveno, both the red and the white varieties, and in those of Bejby in Sweden, the soda is not, as stated by former observers, in excess of the potash. These rocks, consequently, should no longer be regarded as soda-granites.

In the granite of Ulferud, in Sweden, the author finds 74·77 per cent. of silica, 2·65 per cent. of potash, and 4·40 per cent. of soda, thus confirming the results obtained by Hummel and Erdmann. This rock is thus a true soda-granite. In addition to microcline, orthoclase, quartz, muscovite, biotite, zircon, and apatite, it contains a plagioclase-felspar, which gave on analysis the following results:—

SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	Total.	Sp. gr.
67·99	19·23	1·84	1·25	9·69	100·00	2·63

and must therefore be regarded as an almost pure albite.

B. H. B.

Albite in Norwegian Pegmatites. By A. Lacroix (*Jahrb. f. Min.*, 1887, ii, Ref., 455, from *Bull. soc. franç. min.*, **9**, 131—134).—The albite in the pegmatite veins of Moss, Hitterö, and Ytterby is always emplanted on microcline, and is accompanied by quartz, calcite, and a mica differing from the muscovite of the rock. The crystals are poorly developed, the predominating form being $\infty \breve{P} \infty$. Bands of albite contained in the microcline appear to be younger than that mineral. An analysis of the albite of Garta near Arendal gave the following results:—

SiO_2.	Al_2O_3.	Na_2O.	K_2O.	Total.	Sp. gr.
68·40	19·89	10·69	0·90	99·88	2·601

B. H. B.

Griqualandite. By B. H. Brough (*Chem. News*, **56**, 244).—The author shows that the analysis of the supposed new mineral described by Hepburn (Abstr., 1887, 709) as griqualandite, corresponds more closely with the simple formula $H_2O,Fe_2O_3,4SiO_2$, than with the more complicated formula given. The percentage compositions demanded by the two formulæ are—

	SiO_2.	Fe_2O_3.	H_2O.
$H_2Fe_2Si_4O_{12}$..........	57·42	38·28	4·30
$H_{10}Fe_8Si_{16}O_{28}$..........	56·80	37·87	5·33

The formula $H_2O,Fe_2O_3,4SiO_2$ for griqualandite is analogous to that of crocidolite, aegirine, and arfvedsonite, $Na_2O,Fe_2O_3,4SiO_2$. Griqualandite must therefore be regarded as a crocidolite in which hydrogen is substituted for sodium. It is not a pseudomorph after crocidolite, but rather a fibrous hornblende or uralite resulting from the alteration of that mineral. B. H. B.

Mineral Veins. By F. SANDBERGER (*Zeit. Kryst. Min.*, **13**, 409—417).—This memoir is an abstract of the second volume of the author's treatise on mineral veins, in which he brings forward further evidence in support of the lateral secretion theory of the genesis of mineral veins. This theory assumes that water percolating through the country-rock has, by the aid of carbonic acid and other natural solvents, dissolved out of it all the minerals now forming the constituents of mineral veins. The greater portion of the volume is occupied by a discussion of the genesis of mineral veins in crystalline and stratified rocks.

In discussing the tin-ore veins in lithionite-granite, the author applies the term *protolithionite* to a dark lithium mica found in the granite masses of Cornwall, the Erzgebirge, and the Fichtelgebirge. In this mica, as much as 0·22 per cent. of tin oxide has been detected. The deposition of the tin ore, of zinnwaldite, and of turmaline in fissures in the granite is due to the decomposition of this mica. Prosopite is formed by the action of dissolved calcium carbonate on topaz. The fluorine derived from the mica explains the presence of fluorspar in the veins. Tin has also been detected in the potassium-mica of Villeder in Morbihan, and consequently the author regards the tin-ore veins of that district as formed by lateral secretion, whilst he regards the tin ore in the pegmatite of Finbo, in the beds of Pitkäranta and Breitenbrunn, as primitive. At Marienberg in Saxony, tin-ore veins occur in gneiss. In their formation by being dissolved out of the mica in the country-rock, the constituents, silica and tin oxide, least soluble in alkaline carbonates, were deposited first; then followed arsenic and copper; then cobalt and nickel ores, barytes (derived from the orthoclase of the country-rock); and lastly calcite and silver ores. Secondary mica is absent. In the mica of the mica-schist of Ehrenfriedersdorf, which is traversed by tin-ore veins, tin, arsenic, and fluorine have been detected. Lastly, small quantities of tin have been discovered in the phyllites of various districts. In those of Eibenstock and Johanngeorgenstadt, boron has also been found. This discovery enables the formation of interstratified turmaline-schist in these phyllites to be explained. The tin-ore deposits in limestone at Campiglia were undoubtedly derived from an eruptive rock in the vicinity.

The Freiberg gneiss is extremely rich in mica, and in this mineral the majority of the metals occurring in the veins of that district have been detected. The barytes, however, appears to have been derived from the felspar of the country-rock. The metals contained in eruptive rocks of recent age, for instance, in the basalt of Strieth and in the phonolite of Hohenkrähen, segregate in fissures as magnetic or iron pyrites or as hydrated ferric oxide. The ore veins of Transylvania and of America are thought by the author to have been formed in a similar manner by leaching out of the andesites, &c. In the micas of Hungarian rocks, all the metals occurring in the mineral veins are found, whilst fluorine is absent. This is in accord with the known rare occurrence of fluorspar in those veins. The barytes is derived from the anorthic felspar of the country-rocks. At the Comstock lode, the lateral secretion theory has been confirmed by the discovery of the precious metals in the augite of the country-rock. The mineral veins of Caracoles in Jurassic limestone have been derived from the adjacent quartz-trachyte. The metals in this rock are contained for the most part in the hornblende, whilst in the felspar is contained a considerable proportion of barium, which appears in the veins as barytes. B. H. B.

Composition of the Meteorite of Saint-Denis-Westrem. By C. Klément (*Jahrb. f. Min.*, 1888, i, Ref., 45, from *Bull. mus. roy. hist. nat. Belg.*, **4**, 273—282).—The analysis of the meteorite from Saint-Denis-Westrem in East Flanders, gave the following results:—

SiO_2.	Al_2O_3.	Cr_2O_3.	FeO.	CaO.	MgO.	Na_2O.
40·20	2·54	0·90	16·22	2·00	25·08	0·99

Fe.	Ni.	Co.	S.	Total.
10·37	1·24	0·12	2·12	101·78

From these results, the author calculates the following mineralogical composition:—Chrome-iron, ($FeCr_2O_4$), 1·33; iron sulphide, (Fe_7S_8), 5·37; nickel-iron, 8·48; bronzite, 26·18; olivine, 46·41. The remaining 14·01 per cent., which consists of—

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.
7·88	2·54	2·00	0·60	0·99

may perhaps be plagioclase (maskelynite). B. H. B.

Mineral Springs in the Peninsula of Methana. By A. K. Dambergis (*Ber.*, **20**, 3328—3330).—The sulphur springs of Methana rise on the coast on the east side of the Chelona range near the village of Wromolimni, at about the sea level. The temperature of the water—which rises in more than 24 springs forming three separate groups—varies from 26·4° to 31°; the specific gravity of the water varies from 1·02865 to 1·02882. The water, when examined under the microscope, was found to contain the bacteria *Beggiatoa nivea*, often found in sulphurous waters. The water from the various springs showed almost identical composition. The analysis of water from one of the springs gave in parts per 10,000:—NaCl, 297·630; KCl, 6·960; $MgCl_2$, 36·948; $MgBr_2$, 0·584; $CaSO_4$, 21·357; $MgSO_4$, 18·486; $CaCO_3$, 4·600; $MgCO_3$, 2·250; Fe_2O_3, 0·038; Al_2O_3, 0·019; SiO_2, 0·485; organic matter, 0·042; total solids, 389·399. CO_2 as bicarbonate, 3·200; CO_2 free, 7·218; SH_2, 0·109; total mineral constituents, 399·926. Besides this the water contained traces of ammonia, nitric acid, phosphoric acid, iodine, and fluorine. L. T. T.

Analyses of Water from Artesian Wells. By C. KLÉMENT (*Jahrb. f. Min.*, 1888, i, Ref., 71—72, from *Bull. mus. roy. hist. nat. Belg.*, 3, 1—97).—The wells investigated are in Brussels or its immediate vicinity. The bore-holes struck water, below a bed of clay, in fissured chalk underlain by rocks of Silurian age. The following are the depths and temperatures of the water:—1. Hospital St. Pierre, Rue Haute, Brussels, 94·5 m., 15·2°; 2. Distillery, St. Gilles, 65·62 m., 11·8°; 3. Candle factory, Cureghem, 73 m., 12·5°; 4. Godin foundry, Laeken, 106·9 m., 12·5°; 5. St. Sauveur baths, Brussels, 75 m., 12·8°; 6. Boeck brewery, Koekelberg, 115·5 m., 12·0°; 7. Brewery, Anderlecht, 95 m., 12·2°; 8. Starch manufactory, Machelen, 82 m., 12·5°. The analyses were conducted in accordance with Bunsen's method with the following results:—

	1.	2.	3.	4.	5.	6.	7.	8.
$CaCO_3$ ……	0·1343	0·1902	0·0852	0·1084	0·1811	0·0679	0·0998	0·1295
$MgCO_3$ ……	0·0228	0·0740	0·0425	0·0593	0·0976	0·0362	0·0492	0·0686
Na_2CO_3 ……	0·0313	0·0170	—	0·0569	0·0606	0·0653	0·0140	0·0726
K_2NO_3 ……	0·0009	0·0010	0·0020	0·0021	0·0016	0·0014	0·0008	trace
K_2SO_4 ……	0·0388	0·0167	—	0·0256	0·0174	0·0263	0·0374	0·0263
$CaSO_4$ ……	—	—	0·0286	—	—	—	—	—
$MgCl_2$ ……	—	—	0·0174	—	—	—	—	—
NaCl ……	0·0276	0·0063	0·4618	0·0490	0·0020	0·1980	0·4409	0·0102
KCl ……	0·0008	0·0106	0·0433	0·0175	0·0230	0·0177	0·0093	0·0233
SiO_2 ……	0·0324	0·0200	0·0257	0·0300	0·0320	0·0302	0·0258	0·0302
Org. subs. ……	0·0449	0·0179	0·0173	0·0178	0·0135	0·0160	0·0245	0·0115
CO_2 ……	0·0840	0·1295	0·0598	0·1024	0·1559	0·0759	0·0755	0·1231
CO_2 free ……	0·0065	0·0250	0·0274	0·0074	0·0143	0·0032	0·0045	0·0084

B. H. B.

Organic Chemistry.

Preparation of Trimethylene. By G. GUSTAVSON (*J. pr. Chem.* [2], **36**, 300—303).—Trimethylene may be prepared by heating trimethylene bromide with zinc-dust and aqueous alcohol or water; 1 litre of the gas is thus obtained from 10 grams of bromide, and from this quantity of the gas 7·2 grams of dry, crude trimethylene bromide (or 4·57 grams iodide) can be again produced, showing that this method of preparation gives good results.

When trimethylene is passed into concentrated sulphuric acid, liquid hydrocarbons are formed on the surface of the acid, and the solution, after diluting, yields normal propyl alcohol on distillation.

F. S. K.

Conversion of Trimethylene Bromide into Propylene Bromide. By G. GUSTAVSON (*J. pr. Chem.* [2], **36**, 303—304).—When trimethylene bromide and aluminium bromide are placed together in a sealed tube at the ordinary temperature, the former undergoes intermolecular change and propylene bromide is formed.

F. S. K.

Ethylpropylacetylene. By A. BÉHAL (*Bull. Soc. Chim.*, **48**, 216—219).—Butyrone (106 grams) is gradually mixed with phosphorus pentachloride (200 grams), and when the action has ceased a further quantity of butyrone is added and the reaction is completed by heating. The liquid is then cooled and poured on ice, and the chlorine-derivative separated and heated with alcoholic potash in sealed tubes at 130—150° for 20 hours. The product is treated with water and dried over calcium chloride. The ethylpropylacetylene thus obtained is a liquid which boils at 105—106°, and has an odour of acetylene; sp. gr. at $0^\circ = 0·760$.

It does not combine with cuprous chloride, but with mercuric chloride a white precipitate is formed after some time, and when this precipitate is dissolved in dilute hydrochloric acid an odour of butyrone can be perceived.

Bromine acts on it with great energy, yielding a liquid of higher sp. gr. than water. When treated with about twice its own weight of concentrated sulphuric acid at 0°, the hydrocarbon yields a red-brown solution which becomes colourless when mixed with ice. The sole product of hydrolysis is butyrone.

The removal of 2 mols. of hydrogen chloride from dichlorobutyrone may yield diethylallylene, or the corresponding hydrocarbon with a closed chain, but the fact that this hydrocarbon forms a compound with mercuric chloride, and is readily hydrolysed, combined with the absence of tertiary carbon united with the carbon which is in union with the chlorine, render it most probable that this hydrocarbon is ethylpropylacetylene, $CEt \vdots CPr$.

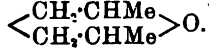
C. H. B.

Hydrolysis of Diallyl. By A. Béhal (*Bull. Soc. Chim.*, **48**, 43—51).—Diallyl is added drop by drop with continual agitation to ordinary concentrated sulphuric acid cooled by ice. The acid becomes red but the colour disappears when the acid is diluted by ice, which is added in sufficient quantity to reduce the temperature, and the product is then neutralised with an alkali or an alkaline earth, preferably the former. The liquid is then distilled and the supernatant layer separated. In all cases the sulphonic acid, $C_6H_{11}\cdot SO_3H$, is obtained. The barium, calcium, and potassium salts are very soluble in water and crystallise with difficulty.

The supernatant layer of the distillate boils at 93°, and is soluble in 15 parts of water at the ordinary temperature. It does not combine with sodium hydrogen sulphite even after prolonged contact, has no action on hydroxylamine, and does not reduce ammoniacal silver nitrate in alcoholic or aqueous solution. It dissolves in hydrochloric acid with development of heat, but no combination takes place; when heated with this acid in sealed tubes at 143—150°, it yields dichlorhydrin boiling at 170—180°. It does not precipitate magnesium chloride solutions, and when treated with phosphorus pentachloride a considerable quantity of hydrogen chloride is evolved, but no definite products could be isolated. Bromine is absorbed with great energy, but the product readily decomposes and cannot be distilled even in a vacuum. In one case the liquid was treated with excess of bromine and then washed with water; when the water was added there was considerable development of heat, and the liquid separated into two layers. The lower layer was hexylene bromide, probably corresponding with pseudohexylene glycol. The upper aqueous liquid readily reduced ammoniacal silver nitrate, and when neutralised and distilled yielded a small quantity of a liquid having the properties of an aldehyde.

The original liquid heated with water at 150—180° yields no glycol.

When hexyl pseudoglycol is mixed with concentrated sulphuric acid at 0°, it yields a product identical with that obtained by the action of the acid on diallyl.

The hydrolysis of diallyl under the influence of sulphuric acid yields a compound formed by the dehydration of isohexyl glycol, identical with the hexylene pseudoxide obtained by Wurtz by the action of silver oxide on diallyl dihydriodide. The oxide thus obtained differs from ordinary glycol by its inaptitude to combine with water, and has the constitution  $<\begin{matrix}CH_2\cdot CHMe\\ CH_2\cdot CHMe\end{matrix}>O$. Its formation is due to the fact that the two alcoholic groups from which the oxide is derived are separated by two atoms of carbon; and the two ethylene-groups do not act independently, but have been linked together by the atom of oxygen, forming an oxide more stable than the glycol. Moreover, the hydroxyl-groups in pseudohexyl glycol are in the γ position, and hence readily form an anhydride.

The other products of the hydrolysis are a sulphonic acid and polymerides of diallyl. C. H. B.

Pyrrolylene Tetrabromide. By G. CIAMICIAN (*Ber.*, **20**, 3061—3064).—The author considers the explanation given by Grimaux and Cloëz (Abstr., 1887, 789) to be improbable.

Hydrocyanic Acid and Cyanogen Iodide. By E. v. MEYER (*J. pr. Chem.* [2], **36**, 292—299). The author confirms Millon's statement that small quantities of hydrocyanic acid prevent the reduction of iodic acid by formic acid, and finds that the hydrocyanic acid causes the iodic acid to assume a passive state, since even when all the former acid has been expelled from the solution by boiling, a certain time elapses before the iodine begins to separate. On the other hand, hydrocyanic acid does not prevent, but only checks, the reduction of iodic acid by sulphurous acid, and a considerable quantity of the latter must be added before the separation of iodine commences. Hydrocyanic acid has no influence on the reduction of iodic acid by hydriodic acid. When a solution of iodine is added to hydrocyanic acid, cyanogen iodide and hydriodic acid are formed up to a certain point, after which the iodine is no longer acted on. These two products have a great tendency to reproduce hydrocyanic acid and iodine, but an excess of hydrocyanic acid prevents this inverse change taking place. Numerous experiments were made to find how much iodine must be added to a constant quantity of hydrocyanic acid in varying quantities of water before free iodine is present in the solution, and the tabulated results show that the amount of iodine used increases with dilution and with the temperature. Cyanogen iodide is completely decomposed by hydriodic acid and sulphurous acid, and these reactions may be employed for the estimation of cyanogen iodide volumetrically. Hydrogen sulphide, stannous chloride, and other reducing agents act in like manner, but towards oxidising agents cyanogen iodide is as stable as iodic acid.

F. S. K.

Oxidation of the Azulmic Matter obtained by the Electrolysis of Ammonia with Carbon Electrodes. By A. MILLOT (*Bull. Soc. Chim.*, **48**, 238—240).—The composition of the black residue obtained by evaporating the liquid after electrolysis (Abstr., 1886, 979), then extracting with alcohol, and finally with water is—C, 35·5; H, 2·0; N, 36·3; O, 26·2. It is not readily oxidised by sodium hypochlorite.

10 grams of the residue was dissolved in water and ammonia, the ammonia expelled by heating on the water-bath, and the gelatinous residue mixed with 50 c.c. of hydrogen peroxide capable of giving 3000 c.c. of oxygen. The mixture was heated on the water-bath for 10 or 12 hours and filtered. On cooling, ammelide is deposited, and on further concentration a second quantity of this compound is obtained. The mother-liquor is evaporated to dryness and extracted with alcohol, which when concentrated deposits crystals of cyanuric acid. The last extracts yield nacreous plates or rhomboïdal prisms of the hydrated acid resembling the modification which Liebig termed cyanilic acid. When this is dissolved in sulphuric acid and precipitated by adding water, it separates in the ordinary form.

That portion of the products of oxidation which is insoluble in alcohol consists of ammonium sulphate, the sulphuric acid having been present as an impurity in the hydrogen peroxide. C. H. B.

Sulphuranes. By E. Braun (*Ber.*, **20**, 2967—2970).—When ethyl sulphurane, $EtS·C_2H_4·S·C_2H_3$, is heated for many hours with excess of ethyl iodide at 100° and the product extracted with water, a crystalline compound is obtained which is either diethylvinylsulphurane or triethylsulphine iodide, whilst the portion insoluble in water yields ethylene bisulphide on fractional distillation.

The diethyl-derivative of ethylene mercaptan, $Et·S·C_2H_4·S·Et$, when treated with ethyl iodide in like manner, is converted into a mixture of triethylsulphine iodide and ethylene bisulphide.

W. P. W.

Propane-derivatives. By C. Winssinger (*Bull. Soc. Chim.*, **48**, 108—112).—The product of the action of bromine on excess of propyl alcohol contains an alcohol which boils constantly at 87°, but has all the other properties of propyl alcohol. After dehydration by means of potassium carbonate, it boils at 92°. It is evident that a hydrate of primary propyl alcohol does actually exist.

Propyl mercaptan and propyl sulphide boil at 67—68° and 141·5—142·5° respectively, under a pressure of 772 mm. Cahours's number, 130—135°, for the boiling point of propyl sulphide was doubtless due to the presence of impurities, one of which was most probably the mercaptan formed in consequence of the partial decomposition of the potassium sulphide into hydrosulphide during the preparation of the derivative. This decomposition becomes much more marked with the higher members in the series.

Orthopropylsulphonic acid is obtained by the action of nitric acid of sp. gr. 1·3 on propyl mercaptan. The reaction is violent, and the first products are nitrogen oxides and a red oil, probably ethyl thioethylsulphonate, which gradually dissolves as the effervescence ceases.

Orthopropyl oxysulphide is obtained by the action of nitric acid of sp. gr. 1·2 on propyl sulphide. It forms long, colourless, and odourless needles, which melt at 14·5—15°, cannot be distilled without decomposition, and dissolve in water, alcohol, and ether. It burns with a brilliant flame, and is easily reduced by ferrous chloride or by nascent hydrogen. When a solution of the oxysulphide and calcium nitrate is concentrated, it yields a fibrocrystalline compound,

$$4[2SOPr_2,Ca(NO_3)_2] + Ca(NO_3)_2,$$

which melts at 80°, and shows the phenomena of supersaturation and superfusion in a very marked manner.

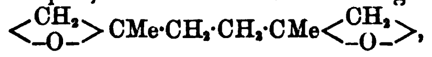
To obtain *diorthopropyl sulphone*, it is necessary to use a warm concentrated solution of potassium permanganate as the oxidising agent. The sulphone crystallises in beautiful, transparent scales, soluble in water, but more soluble in alcohol and ether. It cannot be distilled without decomposition otherwise than in a current of steam.

Monopropylphosphoric acid is contained in the dense viscous residue obtained in the preparation of propyl chloride by the action of phosphorus pentachloride on propyl alcohol. This residue also contains an acid, which yields a barium salt of the composition $PO(OPr)O_2Ba$, anhydrous at 100°, and soluble in cold water, from which it separates on boiling, and an ethereal salt, $PO(OPr)_3$, which is most soluble in water at 70—80°, dissolves in alcohol and ether, and cannot be distilled without decomposition, even in a vacuum. C. H. B.

Synthesis of Diethyl Methyl Carbinol. By A. REFORMATSKY (*J. pr. Chem.* [2], **36**, 340—347).—Diethyl methyl carbinol, $CMeEt_2\cdot OH$, is prepared by the action of zinc on a mixture of diethyl ketone (100 grams) and methyl iodide (495 grams), and subsequent treatment with water. It is a colourless, mobile liquid, having a pleasant smell resembling trimethyl carbinol, boils at 122—123°, and has the sp. gr. 0·8237 at 20°, 0·8194 at 25°, 0·8179 at 30°, and 0·8143 35° (water at 0° = 1). The acetate is a colourless liquid, boiling at 148° (corr.). The iodide boils at 140—144°, and is partly decomposed on distillation. When oxidised with chromic mixture, diethyl methyl carbinol yields acetic acid as the sole product. G. T. M.

Bromination of Allyl Alcohol. By I. FINK (*Monatsh.*, **8**, 561—562).—By bromination of allyl alcohol in absence of water, a dibromhydrin is formed almost in the theoretical proportions, as observed by Markownikoff and v. Tollens. In the presence of water, there is formed in addition a monobromhydrin, $C_3H_7BrO_2$, boiling at 138°, at a pressure of 17 mm.; it is shown to be of this constitution by its conversion into glycerol and triacetin. V. H. V.

Diisobutenyl Oxide. By S. PRZYBYTEK (*Ber.*, **20**, 3239—3246). —The methods of preparation of the following substances have already been given (this vol., p. 123). The dichlorhydrin, $C_8H_{14}Cl_2(OH)_2$, is a thick, viscid, pale-yellow liquid, of faint odour and burning taste.

Diisobutenyl oxide,  $<\overset{CH_2}{\underset{O}{-\!-}}>CMe\cdot CH_2\cdot CH_2\cdot CMe<\overset{CH_2}{\underset{O}{-\!-}}>$, is a colourless, mobile liquid, of agreeable odour and burning taste; it is heavier than water, and boils at 170—180° under 125 mm. pressure. As was to be expected from their respective constitutions, it combines with water with greater slowness and difficulty than does erythrene dioxide.

Octylerythrol, $C_8H_{14}(OH)_4$, is a thick and very viscid liquid, of bitter taste, readily soluble in water and alcohol, but insoluble in ether. It can be formed directly from the chlorhydrin by heating with potash and a large excess of water. A. J. G.

Action of Hydrogen Chloride on Glycerol. By A. FAUCONNIER and J. SANSON (*Bull. Soc. Chim.*, **48**, 236—238).—Dry hydrogen chloride was passed into glycerol for five days, in an apparatus provided with a reflux condenser. The fraction of the product boiling below 80° contains hydrochloric acid and water, together with a small quantity of an oily substance precipitated by water; the fraction 80—120° contains the two dichlorhydrins, in quantity equal to half the weight of the glycerol; the fraction 120—150° contains glyceryl monochlorhydrin, and substances which crystallise in the receiver. The products boiling above 150° have not yet been examined.

The crystalline solid in the last fraction amounts to 0·75 per cent. of the glycerol used. It crystallises from alcohol in white needles, which have the same composition as epichlorhydrin, and melt at 109—110°. The substance is probably a polymeride of epichlorhydrin; it dissolves readily in cold benzene, ether, carbon bisulphide, and chloroform, is somewhat soluble in alcohol, especially on heating, and dissolves slowly in boiling water, from which it crystallises in very long needles. C. H. B.

Sugar-like Nature of Formose. By O. LOEW (*Ber.*, **20**, 3039—3043).—A solution of formose (10 grams) in 1 litre of water is boiled in a reflux apparatus, and the whole extracted with chloroform; the residue obtained by evaporating the chloroform is treated with alcohol, aniline, and a little hydrochloric acid, when an intense red coloration is produced, showing the presence of furfuraldehyde. When formose is digested with 1 per cent. sulphuric acid on a water-bath, more furfuraldehyde is obtained than from other sugars.

Formose has all the following characteristics of sugar:—(1) Sweet taste; (2) strong reducing power; (3) ready decomposition by dilute alkali; (4) formation of saccharic acid by the action of lime; (5) power of combination with hydrogen and hydrogen cyanide, and formation of an osazone; (6) formation of humous substances by acids; (7) formation of furfuraldehyde by dilute acid; (8) capability of fermentation. The author concludes with a criticism of Wehmer's paper on the carbohydrate nature of formose (this vol., p. 40).
N. H. M.

Erythrene Dioxide. By S. PRZYBYTEK (*Ber.*, **20**, 3234—3239). —Erythrene dioxide, when treated with bromine in tubes immersed in cold water, is gradually converted into a citron-yellow, crystalline dibromide, which is insoluble in water, alcohol, and chloroform, and readily decomposes with evolution of hydrogen bromide.

A polymeride of the dioxide is obtained in very small quantities by heating the dioxide at 110—130° (below its boiling point = 137°), a better yield being obtained at 140—150°, but the best yield is obtained when sealed tubes containing powdered anhydrous sodium sulphate just moistened with the dioxide are heated at 110—120° for 10 days. In all cases the polymerisation is very incomplete. It is an amorphous, colourless substance, devoid of taste and odour, and insoluble in water, alcohol, ether, benzene, and chloroform. It can, although with difficulty, be converted into erythrol and its derivatives.

Dihydroxyerythrenedisulphonic acid, $C_4H_6(OH)_2(SO_3H)_2$, is obtained when erythrene dioxide is shaken with a slight excess of concentrated aqueous hydrogen sodium sulphite, and the sodium salt formed decomposed with oxalic acid. It forms a deliquescent mass of felted needles, and is very unstable, charring when gently heated, and yielding sulphurous anhydride when its aqueous solution is heated at 50°. Its salts, on the contrary, are very stable. A. J. G.

Inosite. By LORIN (*Bull. Soc. Chim.*, **48**, 235—237).—The author showed 10 years ago, from its behaviour with oxalic acid, that inosite is a polyhydric alcohol (Abstr., 1878, 398). C. H. B.

Carbohydrates. By Å. G. Ekstrand and C. J. Johanson (*Ber.*, **20**, 3310—3317).—The authors have obtained a new carbohydrate from the haulm of the *Phleum pratense.* The haulm is thickened at its lower end to a bulb and in the autumn this bulb increases in size and becomes filled with a concentrated solution of a carbohydrate to which the authors give the name *graminin.* This substance is a powder resembling starch, of the formula $6C_6H_{10}O_5 + H_2O$, and fuses with decomposition at 215°. It is soluble in water and in caustic potash, insoluble in alcohol. From its aqueous solutions, baryta-water throws down a precipitate which redissolves in excess of the precipitant. It does not give a blue coloration with iodine: it reduces silver nitrate, but not Fehling's solution. Under the microscope, graminin shows spheroïdal granules which are sometimes concentrically striated: on the addition of water a part dissolves, but the larger part remains in the form of half-spheres which show radial striæ. The authors have also obtained graminin from the rhizome of *Baldingera arundinacea,* but in this case a part of the carbohydrate occurs in a less soluble modification. This latter modification shows decided cruciform or semicircular striæ in polarised light. Graminin also seems to be present in the rhizomes of *Calamagnostis agrostis* and of *Teisetum hierochloa.* This carbohydrate seems closely related to inulin and irisin, as is apparent from the following comparison of their properties:—

		Solubility in 100 parts H_2O at ordinary temp.	Rotatory power. $[\alpha]_D$.	Melting point.
Graminin	sol. variety..	3·29 parts	— 48·12°	215°
	insol. ,, ..	1·79 ,,	— 49·27	205
Irisin.................		3·26 ,,	— 52·34	160
Inulin		0·96 ,,	— 34·53	160

From *Dracæna australis* the author has obtained a carbohydrate, $6C_6H_{10}O_5 + H_2O$, which very closely resembles triticin from *Triticum repens.* It differs, however, from the latter in its rotatory power, which is $[\alpha]_D = -36·61°$, whilst that for triticin, is $[\alpha]_D = -41·07°$.

L. T. T.

Inulin. By M. Hönig and S. Schubert (*Monatsh.*, **8**, 529—560).—Braconnot, Berzelius, and Payen have observed the formation of certain dextrins and saccharine substances when inulin is heated; whilst Dragendorff has described intermediate products between inulin and lævulose formed by heating inulin with water under pressure. In this paper, a long account is given of experiments on the saccharification of inulin, effected either by heating inulin in glycerol or with dilute mineral acids: the specific rotatory and cupric oxide reducing powers of the various intermediate products are also set forth in a series of tables. The principal results obtained are as follows:—(1.) The intermediate products obtained by heating inulin with dilute mineral acids, so far as they are directly comparable, seem to be identical with the products obtained by heating inulin by itself. (2.) These dextrin-like substances differ from one another by their specific rotatory power, as also by their solubility in water and alcohol, and their precipitability by barium hydrate. At a lower temperature, the substances formed more nearly resemble inulin as regards their sparing solubility, whilst at a higher temperature, at first certain products, *metinulin* and *inuloid* are produced, which are readily soluble in water, and not precipitated by barium hydrate. After a more profound change, the substance formed shows successively a slight lævorotatory, then no rotatory power, and finally a dextrorotatory power. The specific rotatory power varies from $[\alpha]_j = -41\cdot5$, that of inulin, to $[\alpha]_j = +30\cdot68$, that of the final dextrin. (3.) The substances without specific rotatory power are not identical with lævuloses. (4.) The saccharification of inulin is effected rapidly by dilute acids, reaching its maximum in 15 to 30 minutes, according to the concentration; lævulose and the above-mentioned dextrins are simultaneously produced.

The authors have also succeeded in obtaining lævulose in crystals sufficiently well developed for measurement, by frequently recrystallising the crude crystalline lævulose from absolute alcohol, the crystallisation in each case being induced by dropping in a solid crystal; a similar product was also obtained by the saccharification of inulin. Lævulose crystallises in the rhombic system, individual crystals being of the prismatic and combined crystals of the octohedral type. The axial ratio is $a : b : c = 0\cdot80067 : 1 : 0\cdot90674$, whilst $110 : \bar{1}10 = 77° 22'$ and $011 : 0\bar{1}\bar{1} = 84° 24'$. The crystals are slightly biaxial, resembling, as regards their action on polarised light, certain mixtures of sodium-ammonium and potassium-sodium tartrates. The specific rotatory power of an aqueous solution of the pure lævulose was $[\alpha]_j = -89\cdot74$, $L = 200$ mm., $c = 3\cdot6555$; $t = 22°$. This value when calculated by means of the factor 1·129 gives for $[\alpha]_D$ the value $-87\cdot84°$. Analyses are also given of the pure product, which prove that the formula $C_6H_{12}O_6$ expresses the composition of lævulose.
V. H. V.

Fermentation of Glyceraldehyde. By E. Grimaux (*Compt. rend.*, **105**, 1175—1177).—By oxidising glycerol by means of platinum-black, the author had previously obtained a liquid which seemed to contain glyceraldehyde, although the latter could not be isolated (Abstr., 1887, 695). When this product is distilled in a vacuum with dilute hydrochloric acid, its rotatory power is considerably reduced, and a gummy residue is left which is soluble in absolute alcohol. The residue therefore contains no dextrin, and since dextrose is converted into dextrin under these conditions, it follows that the product of the action of platinum-black on glycerol contains no dextrose. With phenylhydrazine, it yields a compound identical with the hydrazine-derivative obtained by Fischer and Tafel from the products of the oxidation of glycerol by nitric acid. The author oxidised glycerol by Fischer and Tafel's process, neutralised with potassium hydroxide, extracted with alcohol, and evaporated the solution to dryness in a vacuum. The product thus obtained has very little reducing power, but if boiled with very dilute sulphuric acid it recovers its reducing power, and after neutralisation it ferments readily in contact with yeast. Glyceraldehyde is not converted into glucose by treatment with hydrochloric acid.

This is the first instance of the synthetical formation of a sugar which undergoes alcoholic fermentation. It is evident that the property of fermenting in this manner is not confined to carbohydrates containing C_6 and C_{12}. C. H. B.

Decomposition of Nitrosoketones. By H. v. PECHMANN (*Ber.*, **20**, 3213—3214; compare this vol., p. 146).—When boiled with dilute sulphuric acid, fatty nitroketones are converted into hydroxylamine and diketones. When the liquid obtained by treating an alkaline solution of ethyl methylacetoacetate with sodium nitrite and sulphuric acid is distilled with much sulphuric acid, a yellow distillate containing diacetyl is obtained. N. H. M.

Action of Zinc Ethide and Zinc Iodoethide on Dipropylketone. By P. MENSCHIKOFF (*J. pr. Chem.* [2], **36**, 347—352).—Both zinc ethide and zinc iodoethide form condensation-products with dipropyl ketone, but only the compound of the iodoethide yields a tertiary alcohol on treatment with water. G. T. M.

Diacetyl and its Homologues. By H. v. PECHMANN (*Ber.*, **20**, 3162—3164).—By successive treatment with sodium hydrogen sulphite and dilute acids, the homologues of nitrosoacetone are converted into α-diketones (homologues of diacetyl), ammonia and sulphuric acid being also produced. From nitrosomethylacetone, *diacetyl* is obtained: $COMe{\cdot}CMe{:}NOH + H_2SO_3 = COMe{\cdot}CMe{:}NSO_3H + H_2O = COMe{\cdot}COMe + NH_4HSO_4$.

It is a yellowish-green oil which boils without decomposition at 87—88°, and does not solidify when placed in a freezing mixture of ice and salt; its odour resembles that of acetone, and its vapour is the colour of chlorine; it dissolves in 4 parts of water at 15°, forming a yellow solution, and is miscible with ordinary solvents. It is decomposed by alkalis or hot alkaline carbonates, forms a colourless, crystalline substance with ammonia, and with phenylhydrazine yields two hydrazides, melting at 133° and 242° respectively. With aniline, it forms a crystalline product; with orthodiamines, liquid quinoxalines are produced, and it combines readily with alkaline hydrogen sulphites. When reduced in acid solution, it is converted into a benzoïn which reduces Fehling's solution instantly at the ordinary temperature. Since in its physical properties diacetyl differs so considerably from glyoxal, the latter compound must be considered as a polymeric diformyl: diacetyl, however, resembles its higher homologues dibutyl and diisovaleryl. F. S. K.

Chlorinated Methyl Formates. By W. HENTSCHEL (*J. pr. Chem.* [2], **36**, 305—317; compare Abstr., 1887, 1027, 1099).—Trichloromethyl chloroformate, $COCl{\cdot}OCCl_3$, is obtained among other products of the chlorination of methyl chloroformate. When heated at 300°, it decomposes into twice its volume of carbonyl chloride; at a dull-red heat, it yields carbonic anhydride and carbon tetrachloride, whilst in presence of aluminium chloride it is rapidly and completely resolved into these substances, giving almost a theoretical yield of carbon tetrachloride. Both dry and aqueous ammonia convert it into carbamide, but, contrary to the statement of Cahours, no trichloracetamide is formed. If aniline is used instead of ammonia, diphenylcarbamide is formed which, on further treatment with trichloromethyl chloroformate, yields phenyl isocyanate. Trichloromethyl chloroformate does not react with benzene when heated in closed tubes at 150°, but if the substances are brought together in presence of aluminium chloride, triphenylchloromethane is produced. With alcohol and phenol, trichloromethyl chloroformate yields trichloromethyl carbonate, $OMe{\cdot}CO{\cdot}OCCl_3$, and phenyl chloroformate, $COCl{\cdot}OPh$, respectively, whilst it is practically without action on unsaturated hydrocarbons, such as ethylene and amylene, when heated with them in sealed tubes. G. T. M.

Chlorinated Methyl Formates. By W. Hentschel (*J. pr. Chem.* [2], **36**, 468—480).—Trichlormethyl dichlorformate, $C_4H_3Cl_5O_4$ (Abstr., 1887, 1028), is not formed by heating together methyl chloroformate and perchloromethyl formate. By the action of aluminium chloride, the formate is split up into carbonic anhydride, methylene chloride, and chloroform, pointing to the formula

$$CH_2Cl{\cdot}OCCl : O_2 : CCl{\cdot}O{\cdot}CH_2Cl,$$

rather than to $OMe{\cdot}C_2O_2Cl_2{\cdot}O{\cdot}CCl_3$, where chlormethane and tetrachloromethane should be the products.

By distilling the formate (1 mol.) with anhydrous sodium acetate (5 mols.), acetic acid, acetic anhydride, methylene diacetate, and carbonic oxide and anhydride are obtained; if a smaller proportion of sodium acetate is used, acetic chloride and methylene diacetate are formed. The action of aluminium chloride on the formate dissolved in benzene yields di- and tri-phenylmethane. Aniline acts on the formate, producing a crystalline substance, $C_4H_3Cl_3O_4(NHPh)_2$, of unpleasant odour, melting at 45°. By the action of sodium phenoxide on the formate, a phenyl ether corresponding with this anilide was obtained.

On chlorinating methyl chloroformate, a heavy oil, either $C_8H_9Cl_7O_8$ or $C_6H_7Cl_5O_6$, boiling at 180°, is obtained. Its vapour-density could not be ascertained. A. G. B.

Action of Triethylamine on α-Bromobutyric Acid. By E. Duvillier (*Bull. Soc. Chim.*, **48**, 3—6).—When a solution of α-bromobutyric acid (1 mol.) is added to a saturated aqueous solution of triethylamine (2—3 mols.), there is some development of heat, and the liquid separates into two layers, the upper of which is unaltered triethylamine. The mixture is heated to complete the reaction, and the excess of triethylamine distilled off. The products are triethylamine hydrobromide and α-hydroxybutyric acid, the latter being soluble in ether. The barium salt of this acid is almost insoluble in alcohol. The zinc salt crystallises with 2 mols. H_2O in small nodules, which lose their water at 110°. It is almost insoluble in alcohol. No betaïne is formed in this reaction, and hence the behaviour of triethylamine is analogous to that of potassium, barium, or silver hydroxide.

When the dry substances are mixed in the same proportions, there is likewise some development of heat, and the reaction is completed by heating in closed vessels. The products are α-hydroxybutyric acid, traces of crotonic acid, and tetrethylammonium bromide.

C. H. B.

Solubility of Salts of Isovaleric, Methylethylacetic, and Isobutyric Acids. By L. SEDLITZKY (*Monatsh.*, 8, 563—576).—In this paper determinations are given of the solubility of various salts of isovaleric, methylethylacetic, and isobutyric acids, by the method of heating and cooling described by Raupenstrauch; from these determinations, formulæ are deduced, and the calculated results in each case are compared with those found. These formulæ are given below:—

Silver isovalerate, $S = 0{\cdot}1774 + 0{\cdot}003349\,(t - 0{\cdot}2) + 0{\cdot}000006528\,(t - 0{\cdot}2)^2$.

Calcium isovalerate, $S = 18{\cdot}429 + 0{\cdot}10514\,(t - 0{\cdot}2) - 0{\cdot}001091\,(t - 0{\cdot}2)^2$.

Calcium isobutyrate, $S = 20{\cdot}383 + 0{\cdot}08061\,(t - 1) + 0{\cdot}0006522\,(t - 1)^2$.

Silver methylethylacetate, $S = 1{\cdot}1116 + 0{\cdot}0002978\,(t - 1) + 0{\cdot}0002105\,(t - 1)^2$.

Calcium methylethylacetate, $S = 28{\cdot}9822 + 0{\cdot}33186\,(t - 0{\cdot}6) + 0{\cdot}004417\,(t - 0{\cdot}6)_2$.

Barium methylethylacetate could not be obtained in a crystalline form. The curves of solubility in terms of degrees are given in a series of diagrams.

V. H. V.

Oxidation of Palmitic Acid. By M. GRÖGER (*Monatsh.*, 8, 484—497).—An account is given of experiments on the oxidation of palmitic acid with alkaline permanganate, under various conditions of concentration. The principal products formed are acids of the oxalic series, namely, oxalic, succinic, and adipic; acids of the acetic series, namely, acetic, butyric, caproic, and probably caprylic; and acids of the lactic series, namely, hydroxyvaleric and dihydroxypalmitic acids. Other conditions remaining the same, acids of lower molecular weight are produced with greater concentration of the oxidising solution, and acids of higher molecular weight with more dilute solutions. The conditions of each experiment, the products obtained, and the methods by which they were separated, are discussed in detail in the paper.

V. H. V.

Mixed Acid Anhydrides. By W. AUTENRIETH (*Ber.*, 20, 3187—3191).—The general method for preparing the mixed anhydrides consists in heating the acid with two or three times the calculated amount of acetic anhydride in a reflux apparatus for ¼ to ½ an hour. The product is treated with sodium carbonate to remove excess of acetic anhydride as well as the acetic acid; the anhydride separates as an oil from the alkaline liquid.

Acetocaproic anhydride, $C_6H_{11}O\cdot OAc$, is a colourless liquid, which is lighter than water and boils at 165—175°.

Acetovaleric anhydride, $C_5H_9O\cdot OAc$, resembles the above compound; it boils at 147—160°.

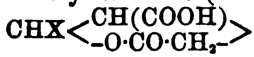
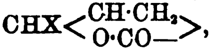
Aceto-β-thioethylcrotonic anhydride, $SEt\cdot CMe{:}CH\cdot CO\cdot OAc$, is a thick yellowish-brown oil, heavier than water, which when exposed to air, gradually decomposes with separation of crystals of thioethylcrotonic acid. It gives a dark-red coloration with sulphuric acid, but does not show the dark-green coloration characteristic of the thioethylcrotonic acids when treated with isatin and sulphuric acid. Nitric acid acts violently on it.

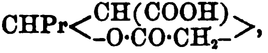
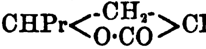
Acetobenzoic anhydride, $COPh\cdot OAc$ (Gerhardt, *Annalen*, **87**, 85), is readily obtained by boiling benzoic acid with acetic anhydride. When treated with ammonia, it is converted, with development of heat, into benzamide and ammonium acetate.

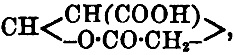
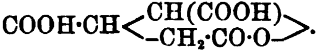
Valerylphenylhydrazide, $NHPh\cdot NH\cdot C_5H_9O$, prepared by mixing acetovaleric anhydride with phenylhydrazine, crystallises in yellowish-white plates melting at 101°; it dissolves readily in alcohol, ether, and chloroform, sparingly in light petroleum.

Capronyl phenylhydrazide, $NHPh\cdot NH\cdot C_6H_{11}O$, crystallises from light petroleum in white needles melting at 116—117° (compare Abstr., 1887, 797).
N. H. M.

Oxidation-products of the α-Hydroxy-acids of the Fatty Series. By V. Aristoff and N. Demjanoff (*Chem. Centr.*, 1887, 1157, from *J. Russ. Chem. Soc.*, 1887, 257—271).—The authors studied the intermediate products which are obtained by oxidising the ethereal salts of the α-hydroxy-acids, on the assumption that the ethereal salts of the ketonic acids formed by that reaction ought to show a greater stability than the ketonic acids themselves. Potassium permanganate was used as the oxidising agent. Ethyl lactate, in sulphuric acid solution, gave ethyl pyruvate. Ethyl hydroxybutyrate gave about 15 per cent. of the theoretical yield of ethyl propionylformate, $CH_3\cdot CH_2\cdot CO\cdot CO_2C_2H_5$. It is thus shown that in oxidising the α-hydroxy-acids, α-ketonic acids are formed as intermediate products.
J. W. L.

Lactones and Lactonic Acids. By R. Fittig (*Ber.*, **20**, 3179—3185).—When the lactonic acids,  $CHX<\begin{matrix}CH(COOH)\\-O\cdot CO\cdot CH_2-\end{matrix}>$, obtained by the union of aldehydes with succinic acid, are boiled, a part distils unchanged, but the greater portion decomposes yielding, as chief products, the monobasic unsaturated acids, $CHX{:}CH\cdot CH_2\cdot COOH$, together with the lactones  $CHX<\begin{matrix}CH\cdot CH_2\\O\cdot CO-\end{matrix}>$, and a small quantity of the anhydride of the bibasic acids, $COOH\cdot CHX\cdot CH_2\cdot COOH$ (?).

Propylparaconic acid,  $CHPr<\begin{matrix}CH(COOH)\\-O\cdot CO\cdot CH_2-\end{matrix}>$, prepared from butyraldehyde and succinic acid, crystallises well, and melts at 73·5°. It readily yields *heptylenic acid*, $C_7H_{12}O_2$, boiling at 224—226°, and heptolactone (Kiliani, Abstr., 1886, 687),  $\mathrm{CHPr}<\begin{matrix}\cdot\mathrm{CH_2}\cdot\\ \mathrm{O\cdot CO}\end{matrix}>\mathrm{CH_2}$. This boils at 232—237° without change, and behaves quite similarly to the other lactones. The abnormal behaviour observed by Kiliani (*loc. cit.*) was probably due to impurity.

Trichloromethylparaconic acid,  $\mathrm{CCl_3\cdot CH}<\begin{matrix}\mathrm{CH(COOH)}\\ \mathrm{-O\cdot CO\cdot CH_2-}\end{matrix}>$, obtained by treating chloral with sodium succinate and acetic anhydride, melts at 97°, and is sparingly soluble. When treated with an excess of baryta-water, it is converted into the barium salt of iso-citric acid. The latter has therefore the constitution $\mathrm{COOH\cdot CH(OH)\cdot CH(COOH)\cdot CH_2\cdot COOH}$; it could not be isolated, as the aqueous solution when evaporated yields the lactonic acid  $\mathrm{COOH\cdot CH}<\begin{matrix}\mathrm{CH(COOH)}\\ \mathrm{-CH_2\cdot CO\cdot O-}\end{matrix}>$. This is crystalline, dissolves in water in all proportions, and gives salts of isocitric acid when treated with bases.

Phenylisohomoparaconic acid, $C_{12}H_{12}O_4$, is obtained together with phenylhomoparaconic acid (Abstr., 1883, 473) by the action of benzaldehyde on methylsuccinic acid; it melts at 124·5°. The two acids react similarly, and when distilled yield phenylbutylenes, unsaturated acids, $C_{11}H_{12}O_2$, and *methylnaphthols*, $C_{10}H_6Me\cdot OH$. The methylnaphthol from methylhomoparaconic acid has probably the constitution [Me : OH = 3 : 4]; it forms yellow needles melting at 89°. The naphthol from the iso-acid is colourless, melts at 92°, and is more stable; the constitution [Me : OH = 2 : 4] is ascribed to it. Both compounds give with bleaching powder a green precipitate, which afterwards becomes yellow. When distilled over heated zinc-dust, they both yield β-methylnaphthalene; this melts at 37—38° (not 32·5°, Schulze, Abstr., 1884, 1184), and has an odour resembling that of naphthalene.

When the tetrabromo-derivative of ethyl ketipate (Fittig and Daimler, Abstr., 1887, 361) is treated with ammonia, alcohol, oxamide (1 mol.) and dibromacetamide (2 mols.) are formed. The constitution of ketipatic acid is therefore $\mathrm{COOH\cdot CH_2\cdot CO\cdot CO\cdot CH_2\cdot COOH}$. The reaction is similar to that observed by Hantzsch and Zeckendorf in the case of ethyl tetrachlorodiketoadipate (Abstr., 1887, 727), which can be prepared by the action of chlorine on ethyl ketipate.

Dimethyldiketone (*Diacetyl*), $\mathrm{COMe\cdot COMe}$, is obtained by distilling ketipic acid. It forms a pure yellow liquid boiling at 87—89°, rather soluble in water, miscible with alcohol and ether. It has an odour resembling that of quinone, and yields a very unstable compound with sulphurous anhydride. The *phenylhydrazine compound*, $C_{16}H_{18}N_4$, crystallises in splendid, slightly yellow needles which melt at 236° with decomposition; it is sparingly soluble in ether, less soluble in alcohol. The *dioxime*, $C_4H_8N_2O_2$, is obtained as a white crystalline precipitate when a dilute solution of the diketone is treated with free hydroxylamine; a very small amount of the diketone can be detected by means of this reaction. The dioxime is very stable, and melts without decomposition at 234° (compare v. Pechmann, this vol., p. 248). N. H. M.

Action of Ammonia on Ethyl Acetoacetate and its Derivatives. By M. CONRAD and W. EPSTEIN (*Ber.*, **20**, 3052—3058).—*Methyl* "*amidoacetoacetate*," $NH_2\cdot CMe\colon CH\cdot COOMe$, is prepared by passing ammonia through a cooled mixture of methyl acetoacetate with ether (2 parts) in presence of powdered ammonium nitrate. It crystallises in lustrous, colourless prisms, a centimetre long, melts at 85°, and sublimes unchanged.

Methyl "*amidoethylacetoacetate*," $NH_2\cdot CMe\colon CEt\cdot COOMe$, is prepared by treating 11·6 grams of methyl acetoacetate with 2·3 grams of sodium and 25 grams of methyl alcohol, and adding ethyl iodide; the whole is afterwards heated on a water-bath; the methyl ethylacetoacetate so obtained boils at 186—188°. This is treated with ammonia, and the crystalline product crystallised from alcohol. It melts at 36—37°.

Ethyl "*amidomethylacetoacetate*," $NH_2\cdot CMe\colon CMe\cdot COOEt$, is prepared by the action of sodium, in the form of wire, on ethyl β-amidocrotonate (m. p. 37°) dissolved in ether, the sodium compound being then warmed with methyl iodide. It is a white, crystalline substance readily soluble in ether, alcohol, and light petroleum; it melts at 52°, sublimes readily, and has a sharp odour and taste. Boiling hydrochloric acid decomposes it very readily into ammonium chloride and ethyl methylacetoacetate.

Ethyl "amidoethylacetoacetate," $NH_2\cdot CMe\colon CEt\cdot COOEt$, is formed by the action of ammonia on ethyl ethylacetoacetate; it was prepared by Geuther. It forms white plates melting at 60°.

Ammonia has no action on ethyl diethylacetoacetate; ethyl "amidoacetoacetate" is therefore probably ethyl amidocrotonate and not an imidobutyrate (compare Kuckert, *Ber.*, **18**, 618). Ethyl dichloroacetoacetate (cooled with ice) is decomposed by ammonia into ethyldichloracetate and acetamide.

Methyl β-amidoethylcrotonate, $NH_2\cdot CMe\colon CMe\cdot COOMe$, melts at 58—59°.

Ethyl "*amidoacetosuccinate*," $NH_2\cdot CMe\colon C(COOEt)\cdot CH_2\cdot COOEt$, crystallises in white, lustrous prisms melting at 72° (compare Brandes, *Jen. Zeitsch.*, **3**, 35). N. H. M.

Action of Aqueous Ammonia on Alkylated Alkyl Acetoacetates, and of Alcohols on the Carboxylic Alkyl-group in Acetoacetates. By T. PETERS (*Ber.*, **20**, 3318—3324).—Brandes (*Jen. Zeitsch.*, **3**, 35, and *Zeit. für. Chem.*, 1866, 437) described the formation of two compounds, $C_7H_{13}O_2N$ and $C_5H_9O_2N$, by the action of aqueous ammonia on methyl ethylacetoacetate. Conrad and Epstein (preceding Abstr.), employing gaseous ammonia, only obtained the compound $C_7H_{13}O_2N$, or methyl amidoethylcrotonate, $NH_2\cdot CMe\colon CEt\cdot COOMe$. The author has repeated Brandes' experiments and, besides $C_7H_{13}O_2N$, obtained ethylacetoacetamide, $CH_3\cdot CO\cdot CHEt\cdot CONH_2$ (m. p. 96°). This is undoubtedly the compound described by Brandes as $C_5H_9O_2N$, and probably obtained by him in an impure state. Ethylic methyl-, isobutyl- and isoamyl-acetoacetates similarly yielded methyl-, isobutyl-, and isoamyl-acetoacetamides, melting respectively at 73°, 85°, and 127°, whilst, if Brandes' supposition is correct that in his experiments the substituted ethyl-group was eliminated, the above three compounds must have yielded amides which were identical.

In preparing methyl ethylacetoacetate the author found that if ethyl alcohol was employed as the solvent, the larger quantity of the methyl salt was converted into the ethyl salt. Making further experiments, he found that isobutyl or isoamyl salts could be readily obtained by the action of the respective alcohol on the ethyl salts, the action taking place especially easily in the presence of a small quantity of sodium. He was similarly able to convert ethyl ethylacetoacetate into the methyl salt in the presence of sodium, but the action was less complete than when replacing a lower by a higher alkyl-group.

L. T. T.

Isomeric Dialkylsuccinic Acids. By C. A. Bischoff (*Ber.*, **20**, 2988—2992).—The author, in conjunction with Voit, has saponified ethyl α-β-dimethylethenyltricarboxylate on the large scale, and has confirmed the results previously obtained by him in conjunction with Rach (Abstr., 1885, 885). In addition, a second acid is also formed which melts at 120°, and is identical with the readily soluble butanedicarboxylic acid (Abstr., 1887, 45), and the product of change from the sparingly soluble dimethylsuccinic acid of high melting points. Voit has also succeeded in converting the two isomeric dimethylsuccinic acids into pyrocinchonic acid.

Two symmetrical diethylsuccinic acids are obtained by saponifying either ethyl diethylacetylenetetracarboxylate or the compound $CEt(COOEt)_2{\cdot}CHEt{\cdot}COOEt$; one of the acids is sparingly soluble, melts at 189°, and can be converted into the second, which is readily soluble, and melts at 127—128°. These acids are probably identical with Hell and Mühlhäuser's isosuberic acids (Abstr., 1880, 542). Experiments are in progress with the object of splitting into two optically active compounds the optically inactive diethylsuccinic acid corresponding with racemic acid. W. P. W.

Symmetrical Diethylsuccinic Acids. By E. Hjelt (*Ber.*, **20**, 3078—3080).—Symmetrical diethylsuccinic acid,

$$COOH{\cdot}CHEt{\cdot}CHEt{\cdot}COOH,$$

is prepared by the action of ethyl α-bromobutyrate on ethyl malonate and sodium ethoxide. The ethyl ethylbutenyltricarboxylate so obtained, which boils at 280—282°, is saponified, and the acid (m. p. 147°) heated at 150°. The residue is then crystallised from hot water, when two acids of the same composition are obtained; the one melts at 189—190°, and is identical with that prepared by Otto by reducing xeronic acid (*Annalen*, **239**, 279), and gives an ethyl salt boiling at 233°, which is identical with that obtained by Hell (*Ber.*, **6**, 30) by the action of silver on ethyl α-iodobutyrate. The second acid melts at 127°. When the acid melting at 189—190° is heated, it is converted into an anhydride which boils at about 240°; when this is boiled with water, it yields the acid melting at 127°. 100 parts of water at 23° dissolve 0·61 part of the acid of higher melting point, and about 2·4 parts of the lower melting acid. The two acids differ also in crystalline form (compare Otto and Rössing, this vol., p. 45).

N. H. M.

Action of Ammonia on Alkyl Salts of Fatty Acids. By S. Ruhemann (*Ber.*, **20**, 3366—3371; compare Trans., 1887, 403).—Phenylhydrazine reacts with ethyl diacetyltartrate, acetylphenylhydrazine being formed. When ethyl diacetyltartaric acid is treated with ammonia, tartramide, $C_4H_8N_2O_4$, is formed. In a similar manner, mucamide is obtained from ethyl tetracetylmucate.

Ethyl aconitate boils at 174—175° under about 22 mm. pressure. When left in contact with aqueous ammonia for 2 to 3 days, it is converted into citrazinamide (*loc. cit.*).

When bromine is added to a solution of citrazinamide in strong hydrochloric acid, the *compound* $C_6H_3Br_3N_2O_3$ separates as a yellow crystalline precipitate. This is stable when dry, but decomposes slowly in presence of moisture; hot water decomposes it with evolution of carbonic anhydride. It dissolves very readily in ammonia and in aqueous potash. The corresponding *chloro-derivative*, $C_6H_3Cl_3N_2O_3$, resembles the bromine compound, but is more stable; it can be crystallised from water, but the solution decomposes when boiled for some time. Both halogen-derivatives react with aniline, orthotoluidine, and piperidine. N. H. M.

Apparatus for Distilling Zinc Methyl and Zinc Ethyl. By A. Kaulfuss (*Ber.*, **20**, 3104—3105).—The apparatus, of which a sketch is given, is so constructed that the distillation can be conducted in an atmosphere of carbonic anhydride. N. H. M.

Disulphones, $R''R'_2(SO_2)_2$ and $R''_2(SO_2)_2$. By R. Otto and R. C. Casanova (*J. pr. Chem.* [2]. **36**, 433—451; compare Abstr., 1885, 261 and 537).—*Ethylenediethyldisulphone*, $C_2H_4(SO_2Et)_2$, is prepared by heating an alcoholic solution of sodium ethylsulphinate (2 mols.) with ethylene dibromide (1 mol.); or by heating an alcoholic solution of sodium ethylenedisulphinate (1 mol.) with ethyl bromide (2 mols.). The identity of the products of these two reactions tends to show that the sulphur in these sulphinic acids is hexavalent. The sulphone crystallises in colourless needles, and melts at 136—137°. Nascent hydrogen in alkaline solution converts it into sodium ethylsulphinate and alcohol. When heated with aqueous potassium hydroxide, it yields a thick oil, which, with benzoic chloride, gives ethylsulphone-ethyl benzoate, $SO_2Et\cdot CH_2\cdot CH_2\cdot OBz$, melting at 118°; the corresponding alcohol could not be isolated.

Ethylenedimethyldisulphone, $C_2H_4(SO_2Me)_2$, is formed when methyl bromide is substituted for ethyl bromide in the above reaction; it crystallises in pearly scales, melts at 190°, and is soluble in hot water.

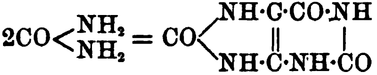
Ethylenedipropyldisulphone, $C_2H_4(SO_2Pr)_2$, forms crystals with a pearly lustre, melting at 155°.

Diethylenedisulphone, $C_2H_4{<}\substack{SO_2\\SO_2}{>}C_2H_4$, prepared by the action of sodium ethylenedisulphinate on ethylene dibromide, is identical with the oxidation product of diethylene disulphide.

Metaphenylenediethyldisulphone, $C_6H_4(SO_2Et)_2$, prepared by the action of potassium benzenedisulphinate on ethyl bromide, forms colourless tables melting at 142°.

Phenylene-ethylenedisulphone, $C_6H_4<\begin{smallmatrix}SO_2\\SO_2\end{smallmatrix}>C_2H_4$, obtained by heating ethylene dibromide with potassium metabenzenedisulphinate, forms very small crystals, insoluble in most solvents. A. G. B.

Synthetical Researches on and Constitution of Uric Acid. By J. HORBACZEWSKI (*Monatsh.*, **8**, 584—593).—The author has shown that uric acid may be synthetically produced from trichlorolactamide and carbamide; it is also formed, although in smaller quantity, from trichlorolactic acid, as also from amidoacetic acid and carbamide. This last change doubtless depends on the intermediate formation of a glycocine-carbamide which reacts with the carbamide to form uric acid, water, and ammonia, thus: $COOH{\cdot}CH_2{\cdot}NH_2,NH_2{\cdot}CONH_2 +$



$$2CO<\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} = CO\begin{cases}NH{\cdot}C{\cdot}CO{\cdot}NH\\ \quad\ \ \| \qquad\quad |\\ NH{\cdot}C{\cdot}NH{\cdot}CO\end{cases} + 2H_2O + 3NH_3.$$

Similarly, methyluric acid may be obtained from sarcosine and carbamide, as also from methylhydantoïn and biuret or amyl allophanate. The formation of uric acid from trichlorolactic acid shows that uric acid is an ureide of acrylic acid, whilst the formation of methyluric acid from methylhydantoïn shows that it is a hydantoïn cyanate. The relation of uric acid to lactic acid is of especial physiological importance, as Minkowski has shown that on removal of the liver from geese, considerable quantities of ammonia and lactic acid occur in the urine, whilst the proportion of uric acid is diminished. It has further been shown by Kanèra and the author that in the human organism the proportion of uric acid is increased by doses of glycerol. On the other hand the synthesis of uric acid from amidoacetic acid is of interest, as v. Knierem has proved that in the organism of birds amidoacetic acid (glycocine) is converted into uric acid and expelled as such in the urine; the same phenomenon has also been observed, to a less degree, in the human organism, since the glycocine is for the most part converted into carbamide. V. H. V.

Furfuracrylic Acid. By H. B. HILL (*Ber.*, **20**, 3359).—Bromine acts on furfuracrylic acid with formation of a crystalline *compound*, $C_7H_6Br_3O_3$, which is decomposed by water into *dibromofurfurethylene* and carbonic anhydride. From the dibromo-compound, monobromofurfuracrylic acid crystallising in long needles, and dibromofurfuracrylic acid can be readily prepared. (Compare Markwald, this vol., p. 135.) N. H. M.

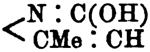
Thiazole Compounds. By A. HANTZSCH and J. H. WEBER (*Ber.*, **20**, 3118—3132, and 3336—3337).—Thiazole is the name given to the isomeric compounds, $<\begin{smallmatrix}N\ :\ CH\\CH:CH\end{smallmatrix}>S$ and $<\begin{smallmatrix}CH\ :\ N\\CH:CH\end{smallmatrix}>S$; no simple thiazole-derivative is known, but by the condensation of certain ortho-benzene-derivatives benzene-thiazoles are formed; for instance, hydroxyphenylthiocyanate gives the compound

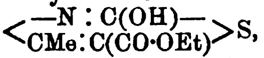
$$C_6H_4{<}\genfrac{}{}{0pt}{}{N}{S}{>}C\cdot OH,$$

and all thiocyanic compounds of ketonic or aldehydic nature in which the carbonyl radicle is in the ortho-position to the thiocyanic group are, in their stable form, thiazole-derivatives, the atomic complex, $CO\colon CH\cdot S\cdot CN$, changing into ${<}\genfrac{}{}{0pt}{}{C\cdot N}{C\cdot S}{>}C\cdot OH$. The term *meso*-derivative is suggested for all compounds in which the hydroxyl-group is displaced. From thiocyanacetone, Tscherniac and Norton (Abstr., 1883, 568) obtained a peculiar base, thiocyanopropimine, to which they gave the formula $NH\colon CMe\cdot CH_2\cdot SCN$; this substance is, however, meso-amidomethylthiazole, ${<}\genfrac{}{}{0pt}{}{N\colon C(NH_2)}{CMe\colon CH}{>}S$; by neither of Hofmann's reactions can it be proved that this compound is a primary amine, and with nitrous acid it yields only resinous products, but from its behaviour towards methyl iodide only two hydrogen-atoms can be in combination with nitrogen; the study of its acetyl-derivatives and of thiocyanacetone prove the above formula to be correct.

Methylamidomethylthiazole hydriodide, $C_4NSH_4\cdot NHMe,HI$, is the principal product of the action of methyl iodide on thiocyanopropimine; it crystallises with 1 mol. H_2O, and when treated with potash yields *methylamidomethylthiazole*; this base is a white, very deliquescent, crystalline substance, not very readily soluble in ether. It has a strongly alkaline reaction, and reacts more readily with methyl iodide than the original base, an abnormal ammonium iodide, $C_{10}H_{14}S_2N_3I$, and *dimethylamidomethylthiazole hydriodide*, being formed. The latter crystallises in large, transparent plates, with 1 mol. H_2O, and melts at 54°, the anhydrous substance melting at 155°; with potash, it yields *dimethylamidomethylthiazole*, which is a crystalline compound and melts at 96°. *Trimethylamidomethylthiazolium iodide*, $C_4NSH_4\cdot NMe_3I$, is obtained on heating the dimethyl base in sealed tubes with methyl iodide; it is a white solid which melts at 85°, and is not decomposed when boiled with potash.

Acetylmethylamidomethylthiazole, $C_4NSH_4\cdot NMeAc$, is produced by acting on the monomethyl base with acetic anhydride; it crystallises in white needles with 6 mols. H_2O, and melts at 50°, the anhydrous compound, however, melts at 113°. The existence of this derivative, and the fact that a diacetyl-derivative cannot be obtained from this compound is strong evidence in favour of the formula suggested, and that thiocyanopropimine is meso-amidomethylthiazole. The acetyl-derivative of amidomethylthiazole forms salts with alkaline hydroxides, the sodium salt, $C_6H_7NaN_2SO + 8H_2O$, is obtained by warming it with concentrated soda. The formation of this compound and the non-formation of a salt in the case of the monomethylacetyl-derivative, are further proofs in favour of the author's formula, as is also the behaviour of dimethylamidomethylthiazole towards bromine; when this last-named compound is treated with bromine-water, only one hydrogen-atom is displaced. The bromo-derivative, $C_6H_9BrN_2S$, crystallises from alcohol and melts at 114°. Amidomethylthiazole and methylamidomethylthiazole are completely destroyed by bromine.

Since thiocyanacetone yields mesoamidomethylthiazole when treated with ammonia, it must be represented by the formula  $<\begin{matrix}N:C(OH)\\CMe:CH\end{matrix}>S$, and not by $COMe{\cdot}CH_2{\cdot}SCN$, that given to it by Tscherniac and Norton (*loc. cit.*). It was obtained by their method in crystalline needles melting at 98°; with phenylhydrazine acetate, hydroxylamine, and sodium hydrogen sulphite, it does not react like a ketone, but with phosphorous pentachloride it acts like a phenol. The hydroxyl-group reacts very readily, and can be displaced by amines; by the action of aniline, *anilidomethylthiazole*, C_4NSH_4NHPh, is obtained; it crystallises from alcohol and melts at 117°. *Paratoluidomethylthiazole* melts at 125°; with metaphylenediamine, the compound, $C_6H_4(NHC_4NSH_4)_2$, melting at 152°, is obtained.

By the action of metallic thiocyanates on ethyl monochloracetoacetate, *ethyl hydroxymethylthiazolecarboxylate*,  $<\begin{matrix}-N:C(OH)-\\CMe:C(CO{\cdot}OEt)\end{matrix}>S$, is formed, a molecular change taking place similar to that occurring in the formation of hydroxymethylthiazole; this ethereal salt melts at 128°, and, judging from its behaviour towards phenylhydrazine, does not contain a ketone-group. A compound, $C_{14}H_{16}O_5N_2S_2$, which melts at 142°, is also formed in this reaction. F. S. K.

Bromobenzenes. By A. J. Leroy (*Bull. Soc. Chim.*, **48**, 210—216).—Benzene, 450 grams, and aluminium chloride, 25 grams, are mixed in a large flask, and the calculated quantity of bromine is added gradually, care being taken to keep the benzene in large excess. The product is treated with dilute hydrochloric acid, separated, and dried. In this way, monobromobenzene is obtained almost free from the diderivative.

Dibromobenzene is obtained in a similar manner, using benzene, 240 grams, bromine, 960 grams, and aluminium chloride, 30 grams. When treated with water, crystals of paradibromobenzene melting at 89° are obtained, together with a small quantity of the tri-derivative, which can be separated by fractionation. The liquid product is mainly dibromobenzene, which boils at 219° and does not solidify at —20°, mixed with some of the monobromo-derivative. The mixture is cooled to remove the para-derivative, and then treated with fuming sulphuric acid and ordinary sulphuric acid, in which the liquid readily dissolves. The product is treated with water to separate the para-derivative, and the liquid is distilled in a current of steam, when metadibromobenzene boiling at 200° is obtained, the yield being equal to about 10 per cent. of the bromine taken. The action of chlorine on benzene, in presence of iodine, yields the ortho- and para-derivatives. With aluminium chloride, no other derivative is obtained. It would seem, therefore, that in the reactions in presence of aluminium chloride there is a tendency to the formation of para- and meta-derivatives.

Paradibromobenzene, when treated with methyl chloride in presence of aluminium chloride, is mainly converted into carbonaceous products; the liquid products, besides monobromobenzene, meta- and paradi-bromobenzene, contain two tribromobenzenes melting at 44° and 119·6° respectively, and yielding nitro-derivatives which melt at 93·5° and 125° respectively.

It would seem that the aluminium chloride first reduces the paradibromobenzene to the monobromo-derivative, part of the bromine becoming free and acting on the mono-derivative with formation of the meta-di-derivative. At the same time, another portion of the liberated bromine forms tri-derivatives. These results are analogous to those obtained by Friedel and Crafts by the action of aluminium chloride on dichlorobenzene. C. H. B.

Action of Sulphuric Acid on Chlorobenzenes. By ISTRATI (*Bull. Soc. Chim.*, **48**, 35—41).—300 grams of pentachlorobenzene was heated with 2000 c.c. of Nordhausen acid for seven to eight hours per day during 15 days. Hydrogen chloride, sulphurous anhydride, and some water, were given off. At the end of 15 days, the acid was decanted off, a fresh quantity added, and the heating continued 15 days longer. No carbonisation took place, but a deep maroon-coloured substance gradually separated. The acid was neutralised by barium carbonate but no sulphonic acid was obtained.

The maroon-coloured substance, after being washed with water, dissolved completely and rapidly in sodium or potassium hydroxide solution, forming a deep red liquid, and when this was filtered and acidified with hydrochloric or sulphuric acid, the substance was reprecipitated. When dried at 60°, it contracts and becomes dark green with a metallic lustre. It is insoluble in boiling water, which removes traces of a colourless, crystalline substance, but it is soluble in concentrated alcohol, very slightly soluble in ether, chloroform, or carbon bisulphide, quite insoluble in benzene. The alcoholic solution, which is cherry-red by transmitted light and yellowish-green by reflected light, and has very great tinctorial power, deposits no solid on cooling, hence it seems probable that a compound is formed. The substance will not crystallise from alcohol, and is not fusible. When heated to redness, it burns and leaves a residue of carbon which is only combustible at a very high temperature. It contains 36·83 per cent. of chlorine, and is free from sulphur. The potassium salt is deep brown with a metallic lustre, and is readily soluble in water, forming a deep red, non-dichroic solution. The barium, iron, tin, mercury, aluminium, magnesium, cadmium, nickel, and other salts, are obtained by double decomposition. They are all pale or deep red, and are insoluble in water, with the exception of the silver salt, which blackens rapidly, and of the mercuric salt, which separates slowly from the solution. The compound seems to have a phenolic function, and the author proposes to call it *Francein*.

Francein is readily attacked and dissolved by cold fuming nitric acid. When heated in sealed tubes at 150° to 180° for six hours, large, colourless crystals, separate. Francein can also be obtained by the action of ordinary concentrated sulphuric acid, and in this case another substance of the same composition as francein, but much more soluble, is also formed at the same time.

Tetrachlorbenzene (200 c.c.), when heated to boiling with concentrated sulphuric acid (1200 c.c.) for 105 hours, is completely dissolved with evolution of water, hydrogen chloride, and large quantities of sulphurous anhydride. No sulphonic acid is formed, but the chief product is a colouring matter which retains a volatile substance; this sublimes at 100°, crystallises in slender needles, and has an odour resembling that of benzoic acid. This substance is removed by treatment with boiling water, when a reddish-brown solid is left easily soluble in alkalis. A considerable portion is soluble in boiling water and especially in alcohol, forming a solution which is pale-brown by transmitted light, and dull-green by reflected light. The more soluble portion contains 33·12 per cent. of chlorine; the portion insoluble in water contains 38·72 per cent.

In the preparation of trichlorobenzenesulphonic acid, when the sulphuric acid is diluted with water, it yields a red product insoluble in water, but easily soluble in alcohol; this is infusible and very dark-coloured with a metallic lustre.

The formation of hydrogen chloride and sulphurous anhydride in these reactions is of special interest. It is probable that under the influence of the sulphuric acid, which plays the part of an oxidising agent, part of the chlorine leaves the benzene nucleus, the sulphuric acid being reduced. This action, which is quite secondary with the lower chlorobenzenes, becomes the dominant reaction with the higher derivatives. In the case of the trichloro-derivative, both reactions are well marked.

When pentachloronitrobenzene is heated with concentrated sulphuric acid, water and hydrochloric acid are given off in large quantities, but very little sulphurous anhydride is liberated. On diluting with water, a crimson precipitate forms. This substance is not soluble in alkalis, but dissolves in warm alcohol from which it separates on cooling. A dilute alcoholic solution is golden-yellow by reflected light and pale-red by transmitted light. C. H. B.

Nitrochlorethylbenzenes. By ISTRATI (*Bull. Soc. Chim.*, **34**, 41—43).—Paradichlorethylbenzene when boiled with concentrated sulphuric acid and fuming nitric acid for 50 hours, fresh nitric acid being added each day, yields a solid, crystalline product completely soluble in the warm acids, from which it is precipitated by adding water. This nitro-derivative is readily soluble in a mixture of alcohol one part and ether two parts. When treated with boiling water, the compound, $C_6H_2Cl_2Et\cdot NO_2$, is dissolved and is deposited on cooling. It is very soluble in alcohol and ether, and crystallises in lamellæ melting at 175°. Its solution is feebly acid, and is not precipitated by lead salts, and is not oxidised by potassium permanganate in the cold. Ferric chloride gives an abundant yellowish-white precipitate.

The portion less soluble in water has the composition $C_6Cl_2Et(NO_2)_3$, and is easily soluble in alcohol, ether, and benzene. It forms small hard crystals which melt at about 195° with partial decomposition. The alcoholic solution mixed with an aqueous solution of ferric chloride yields a slight precipitate after some time.

100 grams of the compound $C_6H_2Cl_2Et\cdot NO_2$ was boiled for 12 hours

with 500 c.c. of fuming nitric acid, and then with a mixture of fuming nitric and sulphuric acids. The product consists of two isomerides which can be separated by treatment with warm alcohol. The less soluble compound forms hard, white crystals which dissolve in ether and melt at 82°. The more soluble compound has a strong aromatic odour and forms crystals melting at 150°. These compounds contain 24 per cent. of chlorine. C. H. B.

Orthocyanotoluene. By S. GABRIEL and B. WEISE (*Ber.*, **20**, 3197—3199).—*Orthocyanobenzal chloride*, $CN{\cdot}C_6H_4{\cdot}CHCl_2$, is prepared by boiling the oil obtained in the preparation of orthocyanobenzyl chloride (Abstr., 1887, 1035), whilst chlorine is being passed through. It boils at 260°. When heated with fuming hydrochloric acid at 170°, orthophthaldehydic acid, melting at 97°, is formed. Strong sulphuric acid converts it into diphthalide ether (m. p. 221°).

Orthocyanobenzotrichloride, $CN{\cdot}C_6H_4{\cdot}CCl_3$, is obtained by the further action of chlorine on the oil from cyanobenzene chloride, and crystallises from alcohol in monoclinic crystals of a vitreous lustre; $a : b : c = 1{\cdot}5464 : 1 : 1{\cdot}1056$; $\beta = 73° 53'$. It melts at 94—95°, and boils at about 280°. N. H. M.

Action of Nitric Acid on Pentamethylbenzene. By M. GOTTSCHALK (*Ber.*, **20**, 3286—3288).—When oxidised with dilute nitric acid, pentamethylbenzene yields *tetramethylbenzenecarboxylic acid*, $C_6HMe_4{\cdot}COOH$ [$COOH : Me_4 = 1 : 2 : 3 : 4 : 5$]. This acid crystallises from alcohol in colourless needles, and melts at 165°. Its *barium salt* crystallises in anhydrous scales or in tufts of needles, $(C_{11}H_{13}O_2)_2Ba + 2H_2O$. When the barium salt is heated with lime, it yields prehnitene. Small quantities of polybasic acids were also formed but were not examined.

When dissolved in cold fuming nitric acid, pentamethylbenzene yields dinitroprehnitene. The author believes that the reaction is analogous to that noticed by Jacobsen (Abstr., 1886, 694), when durene is treated with fuming sulphuric acid, but he has not been able to isolate hexamethylbenzene from the products of the reaction. *Nitropentamethylbenzene*, $C_6Me_5{\cdot}NO_2$, is obtained by the slow action of bromine vapour on a mixture of pentamethylbenzene and silver nitrate at ordinary temperatures. It crystallises from alcohol in long needles melting at 202°. L. T. T.

Phenylacetylene and Diphenyldiacetylene. By A. F. HOLLEMAN (*Ber.*, **20**, 3080—3082).—Phenylacetylene is prepared by boiling monobromocinnamene with alcoholic potash. The bromocinnamene was obtained from ethylbenzene by the method of Friedel and Bahlson (*Bull. Soc. Chim.*, **35**, 55).

Diphenyldiacetylene is prepared by the method of v. Baeyer and Landsberg (*Ber.*, **15**, 57); it melts at 88° (not 97°, Glaser, *Annalen*, **154**, 151). Bromine (4 mols.) acts on diphenyldiacetylene (1 mol.) with formation of a tetrabromide melting at 173°, and a compound melting at 149—153°; analyses of the latter point to the formula $C_{16}H_{10}Br_2{\cdot}C_{16}H_{10}Br_4$. N. H. M.

Iodophenols. By E. NÖLTING and T. STRICKER (*Ber.*, **20**, 3018—3023; compare this Journal, 1874, 259; *Zeit. für Chem.* [2], **4**, 322).—Orthiodophenol remains practically colourless after two years' exposure to the air and light. When treated with nitric acid, iodine is set free, but chloriodophenol is formed if chlorine is passed through its solution in carbon bisulphide. When fused with potassium hydroxide, orthiodophenol yields catechol free from resorcinol, even at temperatures above 250°.

Metiodophenol is formed by the usual reactions from metiodonitrobenzene and metamidophenol; it is necessary to diazotise metiodaniline in an excess of acid, otherwise a compound is obtained which crystallises in red needles, melts at 145°, and is possibly diiodoxyazobenzene, $C_6H_4I{\cdot}N_2{\cdot}C_6H_3I{\cdot}OH$. Metiodophenol crystallises from light petroleum in white needles melting at 39°, or sublimes in small, snow-white needles melting at 40°. It is readily soluble in the usual solvents, does not liberate iodine when treated with chlorine or fuming nitric acid, even when boiled with the latter, and on fusion with potassium hydroxide yields resorcinol free from catechol.

Pariodophenol is readily obtained from paramidophenol. It forms long needles, melts at 93—94°, yields iodine when treated with nitric acid, but not with chlorine, and on fusion with potassium hydroxide at higher temperatures, yields resorcinol instead of quinol.

To explain the formation in fusions with potash or soda of resorcinol from ortho- and para-derivatives, and of catechol from meta-derivatives without assuming the occurrence of intramolecular change, Nölting, recalling the fact that fused alkalis sometimes act as oxidising, and sometimes as reducing agents, suggests that both these actions occur during fusion; 1 : 3 bromophenol, for example, being first oxidised to 1 : 2 : 3 dihydroxybromobenzene, which is then reduced to catechol.

W. P. W.

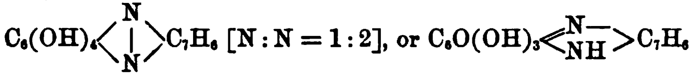
Solid Orthiodophenol from Iodine and Sodium Phenoxide. By C. SCHALL (*Ber.*, **20**, 3362—3364).—When the orthiodophenol obtained by the action of iodine on sodium phenoxide (Abstr., 1883, 1109) is kept for some months, crystals separate, melting at 42—43°. These dissolve sparingly in hot water, and separate as an oil which crystallises when a crystal is added. It then melts at 39—40°. An iodine determination and the vapour-density show that the substance is pure orthiodophenol. The crystals are at first lustrous and transparent, but become slightly red when exposed to air; they are doubly refractive, and are probably monoclinic (compare Neumann, *Annalen*, **241**, 67).

N. H. M.

Occurrence of Catechol in Raw Beet-sugar. By E. O. v. LIPPMANN (*Ber.*, **20**, 3298—3301).—The author has examined a sample of raw beet-sugar which showed a strong reducing action on Fehling's solution, but from its mode of manufacture could not contain invert-sugar. An ethereal extract yielded small quantities of catechol and of an acid, $C_9H_{10}O_4$, which showed most of the properties of catechol, and yielded that substance when heated. The author cannot tell whether these substances were derived from the beetroot, or were formed by the decomposition of part of the carbohydrates during the process of manufacture.

Catechol reduces Fehling's solution, but not Soldaini's solution, and the author therefore advises the use of the latter in preference to Fehling's solution in sugar testing. L. T. T.

Hydroxyquinones. By R. Nietzki and F. Kehrmann (*Ber.*, **20**, 3150—3153).—The authors try to prove experimentally that the formula of tetrahydroxyquinone is, $C_6(OH)_4O_2$ [O : O = 1 : 4], and that of rhodizonic acid, $C_6(OH)_2O_4$ [OH : OH = 3 : 6]. By mixing an aqueous solution of tetrahydroxyquinone with a salt of orthotoluylenediamine, and adding sodium acetate, a green, crystalline substance is precipitated. This dissolves in alkalis and dilute mineral acids; when dried at increased temperatures, it turns brown, and is ultimately converted into the azine of rhodizonic acid; when oxidised it yields diquinoylazine, $C_6O_4{:}N_2C_7H_6$. From its marked basic properties, it was thought that only one nitrogen-atom had entered into reaction, and that its formula was $C_6(OH)_4O{:}NC_7H_6NH_2$, analysis showed, however, that its true composition was $C_{13}H_{10}N_2O_4$, and two formulæ,



$$C_6(OH)_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_7H_6\ [N:N=1:2],\ \text{or}\ C_6O(OH)_3\left\langle\begin{matrix}N-\\NH\end{matrix}\right\rangle C_7H_6$$

[N : NH : O = 1 : 2 : 4], are suggested. Now if tetrahydroxyquinone is an orthoquinone, it would react with diamines even when the hydrogen of the hydroxyl-group is displaced; but with tetrabenzoyltetrahydroxyquinone no reaction takes place. By heating tetrahydroxyquinone with acetic chloride, a yellow, crystalline *diacetyl*-derivative, $C_6O_2(OAc)_2(OH)_2$, is obtained; it melts at 205°, is soluble in alcohol and ether, but less readily in water; it acts like a bibasic acid, and with orthotoluylenediamine yields a compound very similar to that obtained from tetrahydroxybenzene; it is moreover, in its whole behaviour, very similar to chloranilic acid, and has therefore the constitution $[(OH)_2 : (OAc)_2 = 2 : 5 : 3 : 6]$. From these results, it follows that tetrahydroxyquinone is a paraquinone, and that the second of the above formulæ shows the constitution of the compound formed with orthotoluylenediamine. F. S. K.

Dinitrosocresorcinol. By S. v. Kostanecki (*Ber.*, **20**, 3133—3137).—As paraquinon-oximes are obtained by acting on monhydric phenol-derivatives with nitrous acid, it is usually accepted that when more than one isonitroso-group enters into a polyhydric phenol, each takes up the para-position with respect to a hydroxyl-group. The symmetrical formula $C_6H_2O_2(NOH)_2$ $[O_2 : (NOH)_2 = 1 : 3 : 5 : 6]$ has therefore been given to dinitrosoresorcinol, and its correctness is the subject of this research.

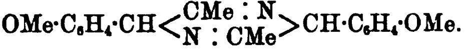
Resorcinol and orcinol give dinitroso-compounds when treated with only one molecule of nitrous acid, but from betorcinol $C_6H_2Me_2(OH)_2$ $[Me_2 : (OH)_2 = 1 : 4 : 3 : 5]$ a mono-derivative only is obtained even with an excess of nitrous acid, and this abnormal behaviour can only be explained by the supposition that the methyl radicle occupies the position which would be taken up by the second isonitroso-group. The formula of dinitroso-orcinol is therefore $C_6HMe(NOH)_2O_2$ [$Me : (NOH)_2 : O_2 = 1 : 2 : 4 : 3 : 5$], and of dinitrosoresorcinol, $C_6H_2(NOH)_2O_2$ [$(NOH)_2 : O_2 = 1 : 3 : 2 : 4$]. These formulæ are supported by the behaviour of cresorcinol, $C_6H_3Me(OH)_2$ [$Me : (OH)_2 = 1 : 2 : 4$], towards nitrous acid, a dinitroso-derivative being produced. Since in cresorcinol there is only one para-position free, it is probable that the symmetrical formula for dinitrosoresorcinol is wrong. *Dinitrosocresorcinol* was obtained in the form of a pale-green substance, which crystallises with 1 mol. H_2O. When heated in a capillary tube above 160°, it explodes; it is sparingly soluble in water and alcohol, insoluble in ether, chloroform, and benzene. Nitric acid oxidises it to *dinitrocresorcinol*, $C_6HMe(NO_2)_2(OH)_2$, which crystallises in long, yellow needles, and melts at 90°, it is sparingly soluble in cold, more readily in hot water, readily soluble in ether or alcohol; it imparts a bright-yellow colour to animal fibres. It is probable that dinitrosocresorcinol has the formula $C_6HO_2(NOH)_2Me$ [$O_2 : (NOH)_2 : Me = 1 : 3 : 2 : 4 : 6$], and that dinitrosoresorcinol has an analogous constitution, namely [$O_2 : (NOH)_2 = 1 : 3 : 2 : 4$]. F. S. K.

Action of Nitrous Acid on Anethoïl. By P. TOENNIES (*Ber.*, **20**, 2982—2987).—The compound of anethoïl and nitrous acid, $OMe\cdot C_6H_4\cdot C_3H_6(N_2O_3)$ (Abstr., 1879, 35, 517), as already described (Abstr., 1881, 167), when heated with alcohol or aqueous potash, yields an isomeric, crystalline product, which dissolves readily in alkalis, but is precipitated by acids from the solution, with the loss of the elements of a molecule of water, in the form of a well-crystallised compound, $OMe\cdot C_6H_4\cdot C\Big<\begin{matrix}CMe\\ N_2O_2\end{matrix}\Big>$. This substance, by the action of alcoholic potash, is converted into an isomeric compound, which readily yields methoxycyanobenzene, $OMe\cdot C_6H_4\cdot CN$, when heated with hydrochloric acid. The compound of anethoïl and nitrous acid, in addition, forms an acetate,

$$OMe\cdot C_6H_4\cdot C(NOAc)\cdot CMeH(ONO),$$

when treated with acetic chloride, and on these grounds is now regarded by the author as an isonitroso-derivative of the formula $OMe\cdot C_6H_4\cdot C(N\cdot OH)\cdot CMeH(ONO)$. The acetate cannot be distilled in a vacuum without undergoing decomposition into acetic acid and the nitrosoketone, $OMe\cdot C_6H_4\cdot C(N\cdot OH)\cdot COMe$, which forms an oil readily crystallising in yellow needles. This compound is easily decomposed by boiling hydrochloric acid, yielding hydroxylamine and the diketone $OMe\cdot C_6H_4\cdot CO\cdot COMe$, which can also be obtained by treating the compound of anethoïl and nitrous acid with hydrochloric acid in the cold; it is a yellow oil, and reacts with phenylhydrazine to form the beautifully crystalline dihydrazide,

$$OMe\cdot C_6H_4\cdot C(N_2HPh)CMe\cdot N_2HPh.$$

The isonitrosoketone is obtained also when the compound of anethoïl and nitrous acid is treated with alcoholic potash, and the product, after the evolution of nitrous oxide has ceased, is dissolved in water and precipitated by hydrochloric acid. On reduction, it is converted into two compounds, one of which is the base $OMe\cdot C_6H_4\cdot CHAc\cdot NH_2$, and the second is the ketone $OMe\cdot C_6H_4\cdot CH_2Ac$, derived from this by loss of ammonia. This ketone is an oil of pleasant odour, boils at 264°, and yields an oily compound with phenylhydrazine. The ketonic base also forms a condensation compound with phenylhydrazine, and is converted into the acetate, $OMe\cdot C_6H_4\cdot CHAc\cdot NHAc$, by the action of acetic anhydride, whilst its solution in hydrochloric acid, if treated with aqueous potash, yields a condensation compound,  $OMe\cdot C_6H_4\cdot CH<\substack{CMe\,:\,N\\N\,:\,CMe}>CH\cdot C_6H_4\cdot OMe$. This tertiary base does not react with acetic acid or nitrous acid, but forms with methyl iodide at 100° a beautifully crystalline hydriodide of a monomethylated base; on heating this it is readily converted into methyl iodide and the original base, but forms with aqueous soda a scarlet-red powder yielding well-crystallised salts with hydrochloric acid and platinic chloride.

The addition product of cinnamene and nitrous acid, $C_2H_3Ph(N_2O_3)$, exhibits properties very similar to those of the anethoïl compounds. By reduction, it yields a base, $C_2H_3Ph(OH)\cdot NH_2$, and on treatment with sulphuric acid, is converted into phenylnitroethylene with the evolution of nitrous oxide. When the cinnamene additive compound is treated with aniline, nitrous oxide is also evolved, and a new base probably of the formula $NHPh\cdot CH(OH)\cdot CPh : NOH$ is obtained; this is decomposed by hydrochloric acid into benzaldehyde, benzonitrile, and aniline. A similar reaction also occurs when ammonia and methylamine are employed instead of aniline, and in this respect the cinnamene compound differs from the anethoïl-derivative, since the latter when treated in like manner with ammonia and methylamine yields, with evolution of nitrous oxide, the diketone,

$$OMe\cdot C_6H_4\cdot CO\cdot COMe,$$

as chief product, only small quantities of the bases

$$OMe\cdot C_6H_4\cdot C(NOH)\cdot CHMe\cdot NH_2,$$

and $OMe\cdot C_6H_4\cdot C(NOH)\cdot CHMe\cdot NHMe$ being obtained. The research is being continued.

W. P. W.

Action of Phosphorous Pentasulphide on Aniline. By A. KNOP (*Ber.*, **20**, 3352—3353). When phosphorous pentasulphide is heated with aniline at a temperature not exceeding 150°, and the product is steam-distilled and crystallised from alcohol, the *compound* $PS\cdot C_{18}H_{18}N_3$ is obtained in monoclinic crystals, melting at 153°; the reaction is accompanied by a violent evolution of hydrogen sulphide.

Chevrier (*Zeit. für Chem.*, 1868, 569), by the action of phosphorus sulphochloride on aniline, obtained an amorphous compound melting at 78°, of the same percentage composition as that described above.

N. H. M.

Sandmeyer's Reaction. Substitution of Cyanogen for the Amido-group. By F. AHRENS (*Ber.*, **20**, 2952—2958).—The three isomeric amidophenols, when diazotised and heated with Sandmeyer's solution of potassium cyanide and copper sulphate (Abstr., 1885, 149), are readily converted into the corresponding cyanophenols (compare next Abstract). To obtain a good yield of orthocyanophenol, it is necessary to separate the diazochloride of orthamidophenol before treatment by Sandmeyer's method, but this step can be omitted in the other two cases. Orthanisidine can in like manner be converted into cyananisoïl.

Paramidoacetophenone, on similar treatment, yields *cyanacetophenone*, $CN\cdot C_6N_4\cdot COMe$. This crystallises in white needles, melts at 60—61°. is insoluble in water, but readily soluble in alcohol and ether, and on hydrolysis is converted into Meyer's acetylbenzoic acid (m. p. = 200°). The *oxime*, $CN\cdot C_6H_4\cdot CMe{:}NOH$, crystallises in white scales melting at 160°. Paramidobenzophenone, under like conditions, forms a *cyanobenzophenone*, $CN\cdot C_6H_4\cdot COPh$, crystallising in yellowish-white granules melting at 107—108°, and this, on hydrolysis, yields parabenzoylbenzoic acid. The *oxime*, $CN\cdot C_6H_4\cdot CPh{:}NOH$, crystallises in white scales and melts at 176°.

When paramidodimethylaniline is similarly treated, and the product extracted with ether, an oil is obtained which could not be purified, but probably consists of dimethylamidobenzonitrile, $CN\cdot C_6H_4\cdot NMe_2$, since, on hydrolysis with alcoholic potash, it yields an acid identical with Michler's paradimethylamidobenzoic acid.

The author has not succeeded in converting sulphanilic acid into cyanobenzenesulphonic acid by this reaction. W. P. W.

Orthocyanophenol. By V. MEYER (*Ber.*, **20**, 3289).—Repeating Ahrens' experiments on the effect of Sandmeyer's reaction on amidophenol, the author entirely failed to get the cyanophenol described by Ahrens (preceding Abstract), but obtained saliconitrile (Tiemann, this vol., p. 276). L. T. T.

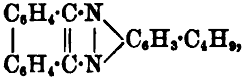
Derivatives of Paramidoisobutylbenzene. By C. GELZER (*Ber.*, **20**, 3253—3259).—*Nitracetylamidoisobutylbenzene*,

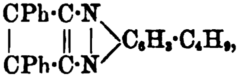
$$C_4H_9\cdot C_6H_3(NO_2)\cdot NHAc,$$

is obtained on nitrating acetylamidoisobutylbenzene at 0°; it crystallises in slender, yellow needles, and melts at 250—252°, with some decomposition. When reduced, an anhydro-base seems to be formed.

Nitramidoisobutylbenzene, $C_4H_9\cdot C_6H_3(NO_2)\cdot NH_2$, prepared by the action of cold alcoholic potash on the acetyl-compound, crystallises in yellowish-red, short needles or plates, melts at 106·5°, is only sparingly soluble in hot water, readily in alcohol, benzene, and ether. The salts are very soluble, and are not characteristic.

Diamidoisobutylbenzene, $C_4H_9\cdot C_6H_3(NH_2)_2$, obtained by the reduction of the preceding compound, crystallises in micaceous, colourless scales or tables, melts at 97·5°, distils at 280—282°, and is sparingly soluble in cold, readily soluble in hot water and in alcohol, ether, and benzene. The *hydrochloride*, $C_{10}H_{16}N_2,2HCl$, forms lustrous, white plates; the *picrate* crystallises in slender, yellow needles; the oxalate forms thin, white plates. Like other orthodiamines, it forms compounds with phenanthraquinone and benzil.

Phenanthraisobutylphenazine,  $\left.\begin{array}{l} C_6H_4\cdot C\cdot N \\ \,|\qquad \|\ \ | \\ C_6H_4\cdot C\cdot N \end{array}\right> C_6H_3\cdot C_4H_9$, prepared by adding the diamido-base to a solution of phenanthraquinone in glacial acetic acid, crystallises in pale-yellow, interlaced needles, melts at 146·5°, and is very sparingly soluble in hot water or cold alcohol, readily in ether or benzene. It is not decomposed when boiled with hydrochloric acid. With concentrated sulphuric acid, it gives a characteristic cherry-red coloration.

Benziloisobutylphenazine,  $\left.\begin{array}{l} CPh\cdot C\cdot N \\ \,|\qquad \|\ \ | \\ CPh\cdot C\cdot N \end{array}\right> C_6H_3\cdot C_4H_9$, forms nearly white, slender needles, melts at 144°, is insoluble in water, moderately soluble in alcohol, and readily in benzene, ether, and carbon bisulphide. It has very feeble basic powers, but a hydrochloride, $(C_{24}H_{22}N_2)_2,HCl$, is described; it forms a greenish, crystalline powder, and is decomposed when dissolved. A. J. G.

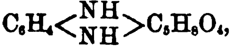
Condensation of Chloral Hydrate with Tertiary Aromatic Amines. By O. Knöfler and P. Boessneck (*Ber.*, **20**, 3193—3195).—The compound, $CCl_3\cdot CH(OH)\cdot C_6H_4\cdot NMe_2$ (Abstr., 1886, 458), is best prepared by treating a solution of 200 grams of chloral hydrate in 300 grams of dimethylaniline with 110 grams of powdered zinc chloride. After some weeks, the viscous mass becomes crystalline. The base is then converted into the hydrochloride. The yield is 82 per cent. of the theoretrical. The *sulphate* crystallises in cubes more soluble than the hydrochloride.

Paradimethylamidobenzylidene-phenylhydrazine,

$$NMe_2\cdot C_6H_4\cdot CH\colon N_2HPh,$$

crystallises in needles melting at 148°.

Paradimethylamidobenzaldoxime, $NMe_2\cdot C_6H_4\cdot CH\colon N\cdot OH$, crystallises in yellowish-brown plates melting at 144°. N. H. M.

Action of Aromatic Diamines on Sugar. By P. Griess and G. Harrow (*Ber.*, **20**, 3111—3118).—*Arabino-orthodiamidobenzene*,  $C_6H_4<\begin{matrix}NH\\NH\end{matrix}>C_5H_8O_4$, is obtained by mixing aqueous solutions of orthodiamidobenzene (1 mol.) and arabinose (2 mols.). The whole is evaporated nearly to dryness, water being added as it evaporates until the amount of crystals no longer increases. It crystallises from boiling water in small, white needles, which melt with decomposition at 235°; it is sparingly soluble in boiling water, less soluble in alcohol, and almost insoluble in ether. It has a slightly bitter taste, does not reduce Fehling's solution, and is dextrorotatory. Aqueous potash dissolves it readily. Boiling concentrated hydrochloric acid and boiling aqueous potash have no action on it. The *hydrochloride* crystallises from water, in which it is readily soluble, in globular groups of very small plates. It is sparingly soluble in dilute hydrochloric acid. The *hydrobromide* resembles the hydrochloride. The formation of arabinodiamidobenzene is similar to that of gluco-orthodiamidobenzene (Abstr., 1887, 930), assuming arabinose to have the formula $C_5H_{10}O_5$ (Kiliani, Abstr., 1887, 465).

Arabinometaparadiamidotoluene, $C_6H_3Me{<}\substack{NH\\NH}{>}C_5H_8O_4$, prepared similarly to the compound above described, crystallises in small, white needles having a slightly bitter taste. It melts at 238°, and is more sparingly soluble than the orthodiamidobenzene-derivative, to which it is in other respects very similar.

Arabino-γ-diamidobenzoic acid, $COOH{\cdot}C_6H_3{<}\substack{NH\\NH}{>}C_5H_8O_4 + 2H_2O$, crystallises in needles melting with decomposition at 235°. It is sparingly soluble in boiling water, less soluble in alcohol. It is dextrorotatory, reddens litmus, and does not reduce Fehling's solution. The barium salt is a white, amorphous substance; the silver salt forms a white, sandy powder. The *hydrochloride* crystallises from dilute hydrochloric acid in small, white needles; it is decomposed by water.

Galacto-orthodiamidobenzene, $C_6H_4{<}\substack{NH\\NH}{>}C_6H_{10}O_5$, resembles the arabino-derivative in physical and chemical properties. It melts at 246° with decomposition. The *hydrochloride* with $1\frac{1}{2}$ mol. H_2O. and the *hydrobromide* crystallise in needles and are very readily soluble in water, sparingly soluble in hydrochloric acid.

Galacto-γ-diamidobenzoic acid, $COOH{\cdot}C_6H_3{<}\substack{NH\\NH}{>}C_6H_{10}O_5 + H_2O$, crystallises in needles. It completely resembles the corresponding arabino-acid. N. H. M.

Decomposition of Diazo-compounds. By I. REMSEN and W. R. ORNDORFF (*Amer. Chem. J.*, 9, 387—399).—Pure and dry diazobenzene nitrate was decomposed by warming it with ten times its weight of absolute alcohol. The several products obtained, calculated on the weight of nitrate taken, were phenetoïl 16 per cent., orthonitrophenol 7 per cent., dinitrophenol 3·5 per cent., benzene 1·8 per cent., and considerable quantities of tarry matter from which nothing definite could be separated; no aldehyde was observed. Griess had previously noticed the production of nitrophenols, and attributed them to his not having used absolute alcohol, but that this explanation is not correct is shown by the above, and by the fact that dry diazobenzene nitrate when heated with dry toluene yields 20 to 24 per cent. of orthonitrophenol, but no dinitrophenol. Using 50 per cent. alcohol for the decomposition, the quantities of nitrophenols formed are increased, whilst the yield of phenetoïl and especially of benzene is decreased. Using dry diazobenzene sulphate and absolute alcohol, 30 per cent. of phenetoïl and 1·5 per cent. of benzene were obtained, and using toluene in place of the alcohol, paraphenolsulphonic acid is formed. The last decomposition, namely, elimination of nitrogen and rearrangement of the constituents of the molecule, corresponds with that undergone by the nitrate:—$C_6H_5{\cdot}N_2{\cdot}O{\cdot}NO_2 = C_6H_4(OH){\cdot}NO_2 + N_2$. Phenetoïl boils at 170°, and when treated with fuming nitric acid yields dinitrophenol (m. p. 86—87°). This is very nearly the melting point of dinitrobenzene (89·9°), and hence the misstatement that benzene is the principal product of the decomposition of diazobenzene with alcohol.

When orthodiazotoluene sulphate is heated with absolute alcohol, the principal product is orthocresyl ethyl ether (30 per cent.); neither toluene nor aldehyde could be detected. With the para-compound, the decomposition is quite different, 18 per cent. of toluene and 11 per cent. of paracresyl ethyl ether being obtained, as well as aldehyde. Metadiazotoluene sulphate and absolute alcohol yield neither aldehyde nor toluene, but metacresyl ethyl ether is formed (55 per cent. reckoned on the metatoluidine employed). The metatoluidine was prepared from paratoluidine by nitrating the acetyl-derivative, eliminating the amido-group, and reducing the metanitrotoluene. In this case, it is to be noticed that the diazo-group is readily displaced by hydrogen, a yield of 68·7 per cent. being obtained.

The authors conclude that the presence of a paraffin residue in the para-position relatively to the diazo-group is favourable to the displacement of the diazo-group by hydrogen. Wroblewski, from a study of the three chlorotoluidines, concludes that in the decomposition of the diazo-compounds by alcohol the normal reaction (production of the hydrocarbon) suffers a change due to the influence of the halogen when it occupies the para-position relatively to some other substituting group. This conclusion is contradicted by the author's experiments. Of the nine recorded cases of mono-substituted amido-benzene compounds that undergo Griess' reaction, eight contain the two groups in the para-position. An examination of the 80 or 90 cases in which two or more groups are present besides the amido-group, and in which the diazo-group is displaceable by hydrogen, also shows that in nearly all cases the amido-group is in the para-position with respect to some other group. H. B.

Diphenylpara-azophenylene. By E. v. BANDROWSKI (*Monatsh.*, 8, 475—483).—In a former paper (Abstr., 1886, 1023), the author showed that the product of the oxidation of diphenylamine in alkaline solution is a diphenylpara-azophenylene, $C_6H_4{<}\begin{smallmatrix}NPh\\NPh\end{smallmatrix}{>}$, a view confirmed by its ready hydrogenation into a leuco-product; the latter seems to be identical with Calm's diphenylparaphenylenediamine. To confirm this view, this substance was prepared according to Calm's directions from quinol and aniline heated with a mixture of zinc and calcium chlorides in a sealed tube at 200—210°. Thus prepared, the melting point of the compound was found to be 132—135°, instead of 152° as assigned to it by Calm. The same melting point was found for the substance $C_{18}H_{16}N_2$, prepared by the author's method; hence there can be no doubt as to the identity of the two compounds in question. This identity was further confirmed by the conversion of the diphenylparaphenylenediamine, prepared by either method, into the oxidation product of diphenylamine, $C_{18}H_{14}N_2$, which was effected either directly by moderate oxidation with hydrogen peroxide, or indirectly by decomposition of the dinitroso-derivative in hot alcoholic solution. This dinitroso-derivative, formed by passing nitrous fumes into a cold alcoholic solution of diphenylparaphenylenediamine, forms yellow, glistening crystals, melting at 120° with decomposition. It gives an intense red coloration with sulphur and nitric acid, and is converted by hydrogenation with zinc-dust and acetic acid, into diphenylpara-azophenylene, and on boiling with alcohol, into diphenylpara-azophenylene and nitric oxide. On bromination in chloroform solution, diphenylpara-azophenylene gives a bromo-derivative,

$$C_{18}H_8Br_6N_2 \text{ or } C_{18}H_{10}Br_8N_2.$$

This forms acicular crystals melting at 243°. It dissolves in nitric acid with production of a dirty-green colour. On dilution a reddish precipitate of a dinitro-derivative is obtained, but this probably consists of two isomeric substances. V. H. V.

Substitution in Azo-compounds. By E. Nölting (*Ber.*, 20, 2992—2998).—Amidoazobenzene yields several crystalline compounds when nitrated, none of which, however, are identical with 1 : 4 or 1 : 3 $C_6H_4(NO_2)\cdot N:N\cdot C_6H_4\cdot NH_2$. The nitro-group seems to enter the amidated group, since aniline was obtained by the reduction of the compound.

When phenylazodimethylaniline (dimethylamidoazobenzene) is dissolved in concentrated sulphuric acid (66° B.), nitrated in a freezing mixture with a mixture of 50 per cent. nitric acid (1 part) and sulphuric acid (2 parts), and the product poured into water, a *nitro*-derivative, $PhN:N\cdot C_6H_3(NO_2)\cdot NMe_2$, is obtained, which crystallises in black needles with a greenish iridescence, and melts at 198°; it is insoluble in water, sparingly soluble in alcohol and ether, readily soluble in benzene. It is a feeble base, and on reduction yields aniline and another base, probably dimethyltriamidobenzene. An isomeric *nitro*-derivative, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe_2$, is also formed, identical with that prepared by Meldola (Trans., 1884, 107). This crystallises in needles, melts at 225—226°, and is sparingly soluble in alcohol, ether, and benzene. On reduction with ammonium sulphide, it yields amidodimethylamidoazobenzene melting at 186—187°, and with tin and hydrochloric acid it is converted into paraphenylenediamine and dimethylparaphenylenediamine.

When paratolylazodimethylaniline is nitrated in like manner, it yields a *nitro*-derivative, $C_6H_4Me\cdot N_2\cdot C_6H_3(NO_2)\cdot NMe_2$, which crystallises in long, bright red needles, melts at 181°, and is sparingly soluble in alcohol and ether, readily soluble in benzene. It is a feeble base, and on reduction is converted into paratoluidine and a readily decomposable base. The isomeric bases, $C_6H_3Me(NO_2)\cdot N_2\cdot C_6H_4\cdot NMe_2$

$$[Me : NO_2 : N_2 = 4 : 2 : 1],$$

crystallising in brownish-red scales melting at 159—160°, and $[Me : NO_2 : N_2 = 4 : 3 : 1]$, crystallising in red prisms melting at 146—147°, were prepared for purposes of comparison.

If phenylazodimethylaniline is sulphonated with 100 per cent. sulphuric acid at 100°, a sulphonic acid, $SO_3H·C_6H_4·N_2·C_6H_4·NMe_2$, is formed, identical with that obtained by Möhlau (Abstr., 1884, 1149). Paratolylazodimethylaniline can be sulphonated by dissolving it in 100 per cent. sulphuric acid and heating at 100° with sulphuric acid containing 66 per cent. of sulphuric anhydride; the resulting sulphonic acid, $SO_3H·C_6H_3Me·N_2·C_6H_4·NMe_2$, crystallises in violet prisms, and is soluble in hot water and alcohol, yielding, like its salts, red-coloured solutions. On reduction, it is converted into dimethylparaphenylenediamine and metamidoparatoluenesulphonic acid. These experiments were made in conjunction with T. Baumann.

When phenylazophenol (oxyazobenzene) is nitrated under the above conditions, the *nitro*-derivative, $NO_2·C_6H_4·N_2·C_6H_4·OH$, forms the chief product. This crystallises in reddish-brown needles, melts at 211°, and is identical with that obtained from phenol and diazotised paranitraniline. The isomeric nitro-derivatives, $[NO_2 : N_2 = 1 : 2]$, crystallising in orange-yellow needles melting at 126°, and $[NO_2 : N_2 = 1 : 3]$, crystallising in red needles melting at 155—157°, were also prepared for purposes of comparison. A *dinitro*-derivative,

$$C_6H_3(NO_2)_2·N_2·C_6H_4·OH,$$

is also formed during the nitration, and constitutes the chief product if twice the quantity of nitric acid is employed. It crystallises in orange-red needles, melts at 200°, and is identical with the compound obtained from diazotised 1 : 2 : 4 dinitraniline and phenol. These experiments were made in conjunction with T. Stricker.

W. P. W.

Diazoamido-compounds. By E. Nölting and F. Binder (*Ber.*, **20**, 3004—3018).—The authors have prepared the diazoamido-compounds from paratoluidine and diazobenzene chloride and from aniline and diazoparatolyl chloride, and have submitted each to the following reactions, comparing the products throughout:—(1.) Reduction at 0° in alcoholic solution with tin and hydrochloric acid: products, aniline, paratoluidine, phenylhydrazine, and paratolylhydrazine. (2.) Bromination in benzene solution in the cold: products, diazoparatoluene bromide and tribromaniline. (3.) Digestion with a mixture of aniline (2 parts) and aniline hydrochloride ($\frac{1}{2}$ part) at 60° until nitrogen was no longer evolved when a sample was treated with dilute sulphuric acid: products, amidoazobenzene and paratoluidine. (4.) Digestion in like manner with dimethylaniline: products, paratolylazodimethylaniline and aniline. (5.) Digestion with excess of phenol and some sodium hydroxide at 60° until nitrogen was no longer evolved when a sample was treated with dilute sulphuric acid: products, phenylazophenol (hydroxyazobenzene) and paratoluidine. The quantity of phenol employed seems to influence the nature of the product (compare Abstr., 1887, 664). (6.) Digestion with excess of dilute sulphuric acid (1 to 10): products, aniline, paratoluidine, phenol, and paracresol. (7.) Ethylation of the compounds, and decomposition of the products by treatment with dilute sulphuric acid: products, ethylaniline, ethylparatoluidine, phenol, and paracresol. In experiments (3) and (5) the compounds act as if each had the constitution $PhN:N\cdot NH\cdot C_7H_7$, in experiments (2) and (4) as if each had the constitution $C_7H_7\cdot N:N\cdot NHPh$, whilst from experiments (1) and (6) both formulæ must be ascribed to each of the compounds, and in experiment (7) each compound must have contained both isomerides, unless in this experiment a third isomeride has been formed, as Meldola has been led to conclude is the case when diazoamidometanitroparanitrobenzene is ethylated (Trans., 1887, 110, 443). In all these experiments, no difference could be detected between the two compounds in the course of the reactions or in the nature or relative quantities of the decomposition products, and hence Griess' conclusion that they are identical is confirmed.

The compounds formed by the action of diazoparatolyl chloride on ethylaniline, and of diazobenzene chloride on ethylparatoluidine are isomeric. *Paradiazotolylethylanilide*, $C_7H_7N:N\cdot NPhEt$, is an oil, which cannot be crystallised, and yields paratolylhydrazine and ethylaniline on treatment with nascent hydrogen, paracresol and ethylaniline on digestion with dilute sulphuric acid, and paratolylazophenol and ethylaniline on digestion with phenol. *Diazobenzene-ethylparatoluide*,

$$PhN:N\cdot NEt\cdot C_7H_7,$$

on the contrary, forms red crystals, melts at 38—39°, and yields phenylhydrazine and ethylparatoluidine on reduction with nascent hydrogen, phenol and ethylparatoluidine on digestion with dilute sulphuric acid, and phenylazophenol and ethylparatoluidine on digestion with phenol.

The compounds formed by the action of diazobenzene chloride on parabromaniline and of parabromodiazobenzene chloride on aniline are identical, and yield parabromaniline and phenol on digestion with dilute sulphuric acid, a result pointing to the formula

$$PhN:N\cdot NH\cdot C_6H_4Br.$$

Diazobenzene chloride reacts with β-naphthylamine to form an amido-azo-compound; a diazo-amido-compound, however, is formed by the action of diazo-β-naphthyl chloride on aniline. This crystallises in bright yellow needles, melts at 150° with decomposition, and yields aniline, β-naphthylamine, phenol, and β-naphthol on digestion with dilute sulphuric acid, amido-azobenzene and β-naphthylamine on digestion with aniline, and phenylazophenol and β-naphthylamine on digestion with excess of phenol, the two last results pointing to the formula $PhN:N\cdot NH\cdot C_{10}H_7$, which does not accord with its method of formation.

The diazo-amido-compound obtained by the action of diazo-α-naphthyl chloride on aniline yields on digestion with dilute sulphuric acid a mixture of aniline, α-naphthylamine, phenol, and α-naphthol.

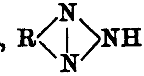
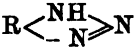
Diazobenzene chloride does not react with paranitraniline. The diazo-amido-compound formed by the action of diazoparanitrobenzene chloride on aniline crystallises in yellow, silky needles, melts at 148°, and yields phenol and paranitraniline on digestion with dilute sulphuric acid, diazobenzene bromide and bromoparanitraniline on bromination, phenylazophenol and paranitraniline on digestion with excess of phenol, and paranitraniline, aniline, amido-azobenzene, and paranitramido-azobenzene, the last in very small quantity, on digestion with aniline.

Diazobenzenepiperide, $PhN\colon N{\cdot}N\colon C_5H_{10}$, obtained by the action of diazobenzene chloride on piperidine and sodium acetate in molecular proportion, yields phenol and piperidine on digestion with dilute sulphuric acid, and phenylhydrazine and piperidine on reduction with nascent hydrogen.

Diazobenzenetetrahydroquinolide, $PhN\colon N{\cdot}N\colon C_9H_{10}$, obtained in like manner, is a yellow oil, and yields phenol and tetrahydroquinoline when boiled with dilute sulphuric acid. *Diazobenzenemethylanilide*, $PhN\colon N{\cdot}NMePh$, also obtained in like manner, is a yellow oil, which gradually changes, especially if traces of acid are present, into the amido-azo-compound, and yields phenol and methylaniline when boiled with dilute sulphuric acid, and phenylhydrazine and methylaniline on reduction with nascent hydrogen. The compound formed by the reduction of paranitrodiazobenzene chloride on methylaniline is *paranitrophenylazomethylaniline*, $C_6H_4(NO_2)N\colon N{\cdot}C_6H_4{\cdot}NHMe$, which crystallises in red needles melting at 134°.

Gasteger has prepared the following:—*Diazoparatolylethylparatoluide*, $C_7H_7N\colon N{\cdot}NEt{\cdot}C_7H_7$, a yellow oil yielding paracresol and ethylparatoluidine with dilute sulphuric acid; *diazometanitrobenzene-ethylparatoluide*, $C_6H_4(NO_2)N\colon N{\cdot}NEt{\cdot}C_7H_7$, which crystallises in yellow needles, melts at 55°, and yields metanitrophenol and ethylparatoluidine when boiled with dilute sulphuric acid; *diazoparanitrobenzene-ethylparatoluide*, $C_6H_4(NO_2)N\colon N{\cdot}NEt{\cdot}C_7H_7$, which crystallises in yellow needles, melts at 114—115°, and yields paranitrophenol and ethylparatoluidine when boiled with dilute sulphuric acid.

W. P. W.

Constitution of Azimido-compounds. By E. Nölting and A. Abt (*Ber.*, **20**, 2999—3003).—Hitherto Griess' formula,  $R\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle NH$ (Abstr., 1883, 56), for the azimido-compounds has been more generally adopted than the alternative formula,  $R\left\langle\begin{matrix}NH\\N\end{matrix}\right\rangle N$, proposed by Kekulé and by Ladenburg (*Ber.*, **9**, 219); the authors, however, bring forward the following evidence in support of the latter, and in addition point out that the formation of acetylazimidotoluene from acetylorthotoluylenediamine (Abstr., 1886, 874) admits of easy explanation on this theory without assuming an intramolecular change, which is necessary if Griess' formula is employed.

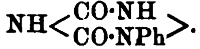
When pure ethyltoluylenediamine hydrochloride [$NEtH : NH_2 : Me = 1 : 2 : 4$] in concentrated aqueous solution is treated at 0° with sodium nitrite in molecular proportion, *ethylazimidotoluene*, $C_6H_3Me\colon N_3{\cdot}Et$, is obtained; this crystallises from alcohol in colourless needles, melts at 147°, and is insoluble in water and alkalis, but soluble in the ordinary organic solvents. The hydrochloride is decomposed by water; the *platinochloride*, $(C_9H_{12}N_3)_2,H_2PtCl_6$, crystallises in yellow needles.

Azimidotoluene (Ladenburg, *ibid.*), prepared in like manner from pure orthotoluylenediamine hydrochloride, has not only basic but feebly acid properties, since it dissolves in alkalis and can be reprecipitated from the solution by carbonic anhydride. The *sodium-compound*, $C_7H_6NaN_3$, crystallises from benzene in white flocks consisting of small needles, and in solution is only stable in the presence of excess of alkali. When ethylated, azimidotoluene yields a compound identical with the ethylazimidotoluene just described, and inasmuch as two isomeric ethyl-derivatives are theoretically possible (assuming Ladenburg's formula), the authors hold that in this case it is the amido-group in the meta-position relatively to the methyl which is converted into the azo-group when orthotoluylenediamine is diazotised. On fusion with potassium hydroxide, azimidotoluene is converted into amidocresol with the evolution of ammonia.

In a footnote, the authors state ethylnitrotoluidine (Gattermann, Abstr., 1885, 975) can be obtained by nitrating ethylacetotoluide in 4 parts of sulphuric acid and subsequently saponifying; if larger quantities (20 parts) of sulphuric acid are employed, appreciable quantities of the meta-derivative are also formed. W. P. W.

Action of Phenylhydrazine on Members of the Carbamide Series.

By S. Skinner and S. Ruhemann (*Ber.*, **20**, 3372—3374).—When biuret is heated over a small flame with a slight excess of phenylhydrazine, ammonia is evolved, and Pinner's phenylurazole (Abstr. 1887, 1042) is formed, to which the authors ascribe the constitution



$$NH<\begin{matrix}CO\cdot NH\\ CO\cdot NPh\end{matrix}>.$$

Diphenylcarbazide, $CO(NH\cdot NHPh)_2$, is prepared by heating urethane (1 mol.) with phenylhydrazine (2 mols.) for some hours, until the evolution of ammonia ceases. It melts at 151°, is readily soluble in alcohol, sparingly soluble in hot water, insoluble in ether.

Phenylsemithiocarbazide, $NH_2\cdot CS\cdot NH\cdot NHPh$, formed by the action of phenylhydrazine on monophenylthiocarbamide, crystallises in white needles melting at 190°, readily soluble in hot alcohol, insoluble in water. Ammonia, nitrogen, benzene, and aniline are formed in the reaction. N. H. M.

Dyes which can be Fixed by Mordants.

By S. v. Kostanecki (*Ber.*, **20**, 3146—3149).—Very little is known of the connection existing between the constitution of organic colouring matters and their tinctorial properties, or what determines whether certain acid colouring matters can be fixed by a mordant or not. Experiments were made which seem to show that nitrosophenols can be fixed by a mordant only when they are *ortho*-quinoneoximes, and that other phenol colours can do so only when they contain two hydroxyl radicles in the *ortho*-position. All the dyes which are derived from gallic acid, for instance, anthragallol, galleïn, coeruleïn, galloflavin, and gallocyanin, owe their tinctorial value to the presence of the ortho-hydroxyl-groups (see also this vol., p. 292). F. S. K.

Products of the Action of Nitric Acid on Acetophenone. By A. F. HOLLEMANN (*Ber.*, **20**, 3359—3362).—Eighty grams of fuming nitric acid (sp. gr. 1·4) is added to 10 grams of acetophenone, and the whole heated at 30—40°; the liquid separates into two layers, of which the upper one becomes crystalline after one to two days. The crystals are washed with water, and extracted with boiling ether. A sparingly soluble nitrogenous substance melting at 177—179° remains undissolved. The ethereal solution yields crystals of a *compound*, $C_2N_2O_2(COPh)_2$, melting at 87°; it is readily soluble in alcohol and ether, insoluble in water. When treated with potash or sulphuric acid, it yields benzoic acid. It is reduced by zinc-dust and acetic acid to diphenylethylene diketone melting at 143° (not 140°). The compound contains no hydroxyl-group, and can be boiled with acetic chloride for a day without change (compare *Rec. Trav. Chim.*, **6**, 60).
N. H. M.

Methyl Duryl Ketone from Asymmetrical and Symmetrical Durene. By A. CLAUS and C. FOECKING (*Ber.*, **20**, 3097—3104).—The durenes are best prepared as follows:—A mixture of 100 grams of mesitylene (or pseudocumene) and 140 grams of methyl iodide is added to 100 grams of aluminium chloride covered with carbon bisulphide, and the whole heated on a water-bath for five days. The product is treated with water, steam distilled, and the distillate fractionally distilled. The three durenes are separated from one another by freezing.

Unsymmetrical duryl methyl ketone, $C_6HMe_4{\cdot}COMe$ [$Me_4 : COMe = 2:3:4:6:1$], is prepared in the usual manner by means of aluminium chloride, and forms a colourless strongly refractive liquid of a peculiar odour boiling at 253—255° (uncorr.); it is readily soluble in the usual solvents except water. It distils without decomposition with superheated steam. The *phenylhydrazine compound* forms lustrous, yellowish, matted needles which decompose at 215° without previous fusion. The *hydroxylamine-derivative* crystallises in small plates melting at 148°. When the ketone is reduced with zinc-dust and alcoholic potash, the *carbinol*, $C_6HMe_4{\cdot}CHMe{\cdot}OH$, is obtained; it is a pale-yellow liquid and boils at above 300°.

2 : 3 : 4 : 6 *Tetramethylphenylglyoxylic acid*, $C_6HMe_4{\cdot}CO{\cdot}COOH$, is formed when the ketone is oxidised with potassium permanganate in dilute aqueous solution in the cold. It is a bright yellow oil, readily soluble in alcohol and ether, sparingly soluble in water. When kept in a freezing mixture for months, it solidifies. Boiling water decomposes it. The *sodium salt* (with 5 mols. H_2O), the *potassium* and *barium* (with 5 mols. H_2O), *calcium* (with 3 mols. H_2O), and other salts were prepared.

2 : 3 : 4 : 6 *Tetramethylmandelic acid*, $C_6HMe_4{\cdot}CH(OH){\cdot}COOH$, is prepared by reducing the glyoxylic acid with sodium-amalgam. It crystallises in short, colourless, transparent, lustrous prisms, melting at 156°; it dissolves readily in alcohol and ether, sparingly in water. The *sodium* (with 1½ mol. H_2O) and *potassium salts* are very readily

soluble in water; the *calcium salt* (with 8 mols. H_2O) crystallises in tufts of needles; the *barium salt* (with 3 mols. H_2O) forms small crystals, readily soluble in water.

Symmetrical duryl methyl ketone, $C_6HMe_4{\cdot}COMe$ [$Me_4 : COMe = 2 : 3 : 5 : 6 : 1$], crystallises in white, lustrous plates, melts at 63° (uncorr.), boils at 251° (uncorr.), and distils with steam. The *hydrazine-derivative* forms small, lustrous crystals which at 225° decompose without melting. The *carbinol* crystallises in white plates which melt at 72°.

Symmetrical durylglyoxylic acid crystallises in small, white, lustrous scales which melt at 124° (uncorr.); it is readily soluble, except in water, and cannot be distilled. The alkali salts are very readily soluble; the *potassium* with 5 mols. H_2O, the *calcium* with 9 mols. H_2O, the *barium* with 3 mols. H_2O, and the *silver salts*, are described.

2 : 3 : 5 : 6 *Tetramethylmandelic acid*, $C_6HMe_4{\cdot}CH(OH){\cdot}COOH$, melts at 146° (uncorr.), dissolves readily in alcohol, ether, benzene, &c. The *alkali salts* are very readily soluble, and can scarcely be obtained crystalline; the *barium salt* with 2 mols. H_2O, and the *calcium salt* with 8 mols. H_2O, were prepared; the latter crystallises in small, slender needles.

2 : 3 : 4 : 6 *Tetramethylbenzoic acid*, $C_6HMe_4{\cdot}COOH$, and the 2 : 3 : 5 : 6 acid are obtained by oxidising the corresponding duryl methyl ketones with warm permanganate solution. The former is a thick oil, whilst the latter crystallises in plates of a silvery lustre, melting at 109° (uncorr.). N. H. M.

Nitrile of Salicylic Acid. By F. TIEMANN (*Ber.*, **20**, 3082—3084).—*Salicylic acid nitrile* is prepared from the aldoxime of salicaldehyde, or by distilling the thiamide of salicylic acid. It melts at 98°, dissolves readily in alcohol and ether, rather sparingly in water, behaves towards alkalis like a phenol, and gives a reddish-violet coloration with ferric chloride; under diminished pressure, it distils almost without decomposition, and can be readily converted into salicylic acid. The compound prepared by Grimaux (*Bull. Soc. Chim.*, **13**, 25) by fusing salicylamide with phosphoric anhydride, which melts at 195°, is therefore not the normal nitrile of salicylic acid (compare also Ahrens, this vol., p. 266). N. H. M.

Condensation-products from β-Anilido-acids. By A. REISSERT (*Ber.*, **20**, 3105—3110).—*β-Anilido-acrylic acid*, $NHPh{\cdot}C_2H_2{\cdot}COOH$, is obtained by boiling the mixture of anilidomaleïc-anilide and anilidomaleïc acid (formed from aniline and dibromosuccinic acid, Tiemann and Reissert, Abstr., 1886, 551; Michael, Abstr., 1886, 698; and Reissert, Abstr., 1886, 791), with aqueous potash. The product is precipitated with acetic acid, dissolved in absolute alcohol, and converted into the sodium salt. It melts with partial decomposition at 194°, dissolves readily with alcohol and acetone, and is almost insoluble in water, benzene, and chloroform. The *sodium salt* with 2½ mols. H_2O crystallises in white plates of a silky lustre; the *ethyl salt* melts at 143—144°.

γ-Ketodihydroquinoline, $C_6H_4<\genfrac{}{}{0pt}{}{CO\cdot CH}{NH\cdot CH}>$, is formed when β-anilidoacrylic acid is dissolved in concentrated sulphuric acid, or when the acid is heated for a short time at 200°. The product is several times dissolved in acetone and precipitated with water, and is then crystallised from alcohol, from which it separates in gold-coloured plates melting at 235°. When distilled, a small amount is obtained colourless. It is very sparingly soluble in the usual solvents, and is almost insoluble in acids and alkalis. When distilled over heated zinc-dust, quinoline is formed. N. H. M.

Formation of Anilic Acids from Anhydrides of Bibasic Acids. By R. ANSCHÜTZ (*Ber.*, **20**, 3214—3216).—Fumaranilic acid, $COOH\cdot CH\colon CH\cdot CO\cdot NHPh$, identical with that prepared from maleïnanil, is formed when maleïc anhydride, dissolved in ether, is mixed with aniline.

Mesaconanilic acid, prepared from citraconic anhydride, melts at 152—153°, and is identical with the product which separates when an aqueous solution of monaniline citraconate is kept.

The anilic acid from itaconic anhydride melts at 151—151·5°; it is not identical with the acids obtained by Gottlieb and by Michael by heating itaconic acid with aniline, and by boiling an aqueous solution of monaniline itaconate. N. H. M.

Hydrazocumic Acid. By N. MOLCANOFFSKI (*Chem. Centr.*, 1887, 1162, from *J. Russ. Chem. Soc.*, 1887, 295—297).—Nitrocumic acid was reduced in alkaline solution by an excess of sodium amalgam and the reduction products (mostly the azo- and hydrazo-acids) precipitated by adding hydrochloric acid. They were separated by crystallisation from alcohol, the hydrazo-acid being much less soluble in this medium. *Hydrazocumic acid* forms colourless needles, very stable when dry, but in solution slowly changing into the azo-acid, nearly insoluble in cold alcohol, more readily soluble in hot alcohol, still more readily in hot methyl alcohol, insoluble in ether. Nitric acid reacts with it in the same way as with the azo-acid. When heated with concentrated hydrochloric acid in sealed tubes at 100—115°, it partly dissolves with a violet colour. From the solution, a white crystalline substance separates after some time which is easily soluble in alcohol, dilute hydrochloric and nitric acids, and in concentrated sulphuric acid. Salts of the azo-acids crystallise out from the solution of the hydrazo-acids in alkalis, and these effloresce when exposed to the air. The sodium salt contains 12 mols. H_2O.

J. W. L

Synthesis of Phenoxycoumarin. By A. OGLIALORO (*Chem. Centr.*, 1887, 1164, from *Rend. Acc. Sc. Napoli* [2], 1, 90—91).—The author has already shown that phenylcoumarin is formed by the action of sodium α-toluylate on salicaldehyde and acetic anhydride (Abstr., 1880, 164), and phenoxycinnamic acid by the action of sodium phenylglycolate on benzaldehyde and acetic anhydride, (Abstr., 1881, 276). By heating acetic anhydride (100 grams) salicylaldehyde (25 grams) and sodium phenylglycolate (40 grams) for eight hours at 150—160° *phenoxycoumarin*, $C_{15}H_{10}O_3$, is formed. It crystallises in small, yellow prisms, melts at 113° (uncorr.), is nearly insoluble in cold, very sparingly soluble in hot water, more readily in alcohol, sparingly in ether and light petroleum, very readily in chloroform and benzene. An alkaline extract from the crude product of the reaction when acidified gave a brown precipitate that crystallised slowly. From this an acid, crystallising in yellow needles and melting at 175° with decomposition, could be separated, but has not yet been fully investigated. J. W. L.

Derivatives of Ethyl Quinoneparadicarboxylate. By A. HANTZSCH and A. ZECKENDORF (*Ber.*, **20**, 2796—2801).—The compound $C_{12}H_{12}Cl_2O_6$, obtained by the hydrogenation of ethyl dichloroquinonedicarboxylate (Abstr., 1887, 727), was shown by Lehman, as quoted by the authors (*Ber.*, **20**, 1313), to exist in two forms. The first of these crystallises in colourless, radially grouped needles destitute of fluorescence, and melts at 123° to a green liquid; the second, formed from the preceding by rapid cooling of the fused substance, crystallises in greenish-yellow, dichroic tables which are stable at the ordinary temperature, but are very readily transformed by gentle heating into the original colourless needles. The former represents the stable modification, and is regarded as *ethyl dichloroquinoldicarboxylate*, $C_6(OH)_2Cl_2(COOEt)_2$, whilst the latter is the labile form, and is regarded as *ethyl dichloroquinonedihydrodicarboxylate*,

$$C_6H_2Cl_2O_2(COOEt)_2.$$

In the case of the compound $C_{12}H_{14}O_6$, from which the compound $C_{12}H_{12}Cl_2O_6$ is derived by chlorination and hydrogenation, the order is reversed, ethyl quinonedihydrodicarboxylate, the coloured compound, being the stable and ethyl quinoldicarboxylate, which is colourless, the labile form (*ibid.*). It is now shown that the dichloro-acid corresponding with these salts also exists in two modifications—one coloured and the other colourless.

When colourless ethyl dichloroquinoldicarboxylate is treated in the cold with concentrated aqueous soda, a greenish-yellow sodium salt is obtained. In aqueous solution, this also is greenish-yellow, and yields the unaltered ethyl salt on treatment with hydrochloric acid. If, however, the alkaline solution is saponified on a water-bath, evaporated nearly to dryness, and the sparingly soluble residue dissolved in water and acidified, a pale yellow solution is obtained which by rapid evaporation yields *dichloroquinonedihydrodicarboxylic acid*,

$$C_6H_2Cl_2O_2(COOH)_2 + 2H_2O,$$

in the form of greenish-yellow needles. These are stable in the air, but effloresce on exposure over sulphuric acid, yielding *dichloroquinoldicarboxylic acid;* the stable form, is a white, anhydrous powder, which on heating carbonises without fusion or change of colour, is sparingly soluble in alcohol and ether, almost insoluble in water, and passes into the labile form only by heating with aqueous soda and acidifying the solution, since it does not directly combine with the elements of water.

Hitherto compounds of this type have been known to react as if they possessed only one of the two formulæ ascribed to them. An examination of ethyl tetrahydroxyterephthalate (Abstr., 1886, 1028) shows, however, that it sometimes reacts as if it were this compound, and at others as if it had the composition of the yellow, stable ethyl dihydroxyquinonedihydrodicarboxylate, $C_6H_2(OH)_2O_2(COOEt)_2$. Thus, when heated with acetic anhydride, it is converted into a *tetracetyl*-derivative, $C_6(OAc)_4(COOEt)_2$, a white, microcrystalline powder melting at 202°. If, however, the yellow salt is dissolved in concentrated aqueous ammonia and treated with hydroxylamine, it yields the *dioxime* of ethyl dihydroxyquinonedihydrodicarboxylate, $C_6H_2(OH)_2(NOH)_2(COOEt)_2$, as a yellow powder melting at 156—157° without decomposition, and soluble in alkalis and ammonia. The very similar yellow, stable ethyl quinonedihydrodicarboxylate, on the contrary, does not react with hydroxylamine under the conditions just stated, but yields a colourless *diacetyl*-derivative of ethyl dihydroxyterephthalate when heated with acetic anhydride. Moreover, the compound $C_6H_2O_4(COOEt)_2$ (Abstr., 1886, 354) reacts as if it were ethyl dihydroxyquinonedicarboxylate, since it yields with hydroxylamine the *dioxime*, $C_6(OH)_2(NOH)_2(COOEt)_2$; this is a yellow powder, which melts at 160° with decomposition, and is very sparingly soluble in alcohol and ether, soluble in hot chloroform and acetic acid.

When ethyl succinosuccinate is treated with bromine in molecular proportion, and particularly when the bromination proceeds rapidly, a compound which crystallises in yellow needles is present in the mother-liquor from ethyl quinonedihydrodicarboxylate. This is a *hydrate* of ethyl quinonedihydrodicarboxylate, $C_{12}H_{14}O_6 + 2H_2O$. It melts at 113°, and is slowly converted into the anhydrous compound by recrystallisation, or more rapidly by boiling its alcoholic solution. In its fluorescence, colour reactions with ferric chloride, &c., it resembles the anhydrous salt, but differs from it by yielding, on treatment with hydroxylamine in ammoniacal solution, *ethyl quinoltetrahydrodicarboxylate*, $C_6(OH)_2H_6(COOEt)_2$, a yellow, crystalline substance melting at 128°. W. P. W.

Preparation of Orthosulphobenzoic Acid. By N. R. BRACKETT and C. W. HAYES (*Amer. Chem. J.*, **9**, 399—406).—The preparation of orthotoluenesulphonic acid from paranitrotoluene by the diazo-reaction is not satisfactory, as the greater portion is converted into an ethoxy-compound. Haller's method (decomposition of the hydrazine compound by copper sulphate) is much better. *Hydrazine orthotoluenesulphonic acid*, $N_2H_3{\cdot}C_6H_3Me{\cdot}SO_3H$, prepared by the usual methods, crystallises in scales, is soluble in hot water, and has acid properties. With copper sulphate, it decomposes readily, but the orthotoluenesulphonic acid is not easily purified, and is not readily oxidised by potassium permanganate except in alkaline solution; moreover the yield of the benzoic acid is not satisfactory. Again, sodium orthotoluenesulphonate as prepared above does not give a good yield of orthotoluenesulphonamide, and this last when oxidised gives a fair yield of the sulphinide, but little of orthosulphobenzoic acid.

The best and quickest method of preparing this compound is that of Noyes (Abstr., 1886, 804) by the action of chlorosulphonic acid on toluene; a mixture of the para- and ortho-compounds is obtained which is best converted by ammonium carbonate into the toluenesulphonamides; by treatment with potassium permanganate the para-compound is oxidised to parasulphobenzoic acid, and is precipitated by addition of dilute hydrochloric acid, whilst from the filtrate strong hydrochloric acid throws down the orthobenzoic sulphinide. This may then be converted into orthosulphobenzoic acid by evaporating with hydrochloric acid; the residue is extracted with water, from which the substance separates in large rhombic crystals; $a : b : c = 0{\cdot}5507 : 1 : 0{\cdot}8121$.

H. B.

Paramido-orthosulphobenzoic Acid. By W. A. Hedrick (*Amer. Chem. J.*, 9, 410—418).—Paranitro-orthotoluenesulphonic acid is oxidised by potassium permanganate in alkaline solution, and the paranitro-orthosulphobenzoic acid precipitated from the filtered and concentrated solution by hydrochloric acid. The reduction of the nitro-group is effected by ammonia and sulphuretted hydrogen; the yield of the pure amido-acid amounts to one-half the weight of the nitrotoluene used. The following salts are described: $[COOH{\cdot}C_6H_3(NH_2){\cdot}SO_3]_2Ba + 5H_2O$; $C_7H_5NSO_5Ba + H_2O$; $C_7H_5NSO_5Pb$; and $C_7H_5NSO_5Ag_2$. The silver salt, when boiled with methyl iodide, and then with water and calcium carbonate, yields a compound, $NMe_2{\cdot}C_6H_3{<}{}^{COO}_{SO_3-}{>}Ca$, whilst ethyl iodide and barium carbonate yield a neutral salt,

$$[COOEt{\cdot}C_6H_3(NH_2){\cdot}SO_3]_2Ba.$$

The free amido-acid has no basic properties, and no acetyl or benzoyl compound could be obtained from it.

Paradiazo-orthosulphobenzoic acid, $COOH{\cdot}C_6H_3{<}{}^{N_2-}_{SO_3}{>}$, is best obtained by passing nitrous anhydride into a solution of the acid barium salt containing some of the same salt in suspension; it separates in white crystals. It may be converted into a well-crystallised hydrazine-compound in the usual way. The diazo-compound when boiled with water yields *hydroxysulphobenzoic acid*, of which the following salts are described:—

$$[COOH{\cdot}C_6H_3(OH){\cdot}SO_3]_2Ba,\ (C_7H_3SO_6)_2Ba_3,\text{ and }C_7H_4SO_6Ca + 5H_2O;$$

the last salt crystallises in the triclinic system; $a{\cdot} : b : c = 0{\cdot}9567 : 1 : 1{\cdot}0121$; observed faces: $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, ∞P, and $0P$.

H. B.

Metacresolsulphonic Acids. By A. Claus and J. Krauss (*Ber.*, 20, 3089—3095).—*Metacresolparasulphonic acid*,

$$OH{\cdot}C_6H_3Me{\cdot}SO_3H\ [OH : Me : SO_3H = 1 : 3 : 4],$$

is obtained by heating sulphuric acid and cresol (equal weights) at 100—120° for some hours. The reaction also takes place at the ordinary temperature, but requires three or four days. It crystallises from dilute sulphuric acid in colourless plates (with 2 mols. H_2O)

melting at 75° (uncorr.), and from concentrated sulphuric acid in large, colourless plates (with $1\frac{1}{2}$ mol. H_2O) which melt at 95—96° (uncorr.). The anhydrous acid melts at 118°, and dissolves very readily in water, alcohol, ether, and benzene. The potassium salt (with $2\frac{1}{2}$ mols. H_2O) forms stellate groups of small crystals of a fatty lustre readily soluble in water; the *sodium* and *lead salts* are also readily soluble in water. The *copper salt* (with 3 mols. H_2O) crystallises in tufts of lustrous, pale-yellow prisms rather readily soluble in water. The *sulphochloride*, $C_7H_7O{\cdot}SO_2Cl$, forms a thin, honey-coloured syrup. The *sulphonamide* is readily soluble in alcohol and ether; it does not crystallise. When a dilute solution of the sulphonic acid is heated with chromic acid, toluquinone is formed.

Metacresoldisulphonic acid is prepared by heating metacresol with sulphuric acid (4 to 6 parts) at 120—140° for some hours, and forms an oily liquid readily soluble in water and alcohol, soluble in ether and benzene. The *potassium salt* crystallises with 3 mols. H_2O in colourless plates of a fatty lustre; the *barium salt* (with $\frac{1}{2}$ mol. H_2O) is very readily soluble; the *lead salt* is a readily soluble, slightly lustrous, crystalline powder. The *copper salt* is extremely soluble. The *disulphochloride* is a thick, honey-coloured liquid. The *disulphonamide* is also a syrup.

Metacresoltrisulphonic acid is formed when the cresol is heated with fuming sulphuric acid and phosphorus pentoxide at 180°. The *barium salt* is very readily soluble in water. N. H. M.

Orthocresolsulphonic Acids. By E. Hantke (*Ber.*, **20**, 3209—3213).—When orthocresol is heated with sulphuric acid for five to six hours on a water-bath, Engelhardt and Latschinoff's sulphonic acid (*Zeitsch. f. Chem.*, 1869, 621) is formed. The potassium salt crystallises with $\frac{1}{2}$ mol. H_2O. The acid has the constitution—

$$[Me : OH : SO_3H = 1 : 2 : 4].$$

The same acid is formed together with Neville and Winther's sulphonic acid, $[Me : OH : SO_3H = 1 : 2 : 5]$ (*Ber.*, **13**, 1946), when orthocresol is treated with sulphuric acid in the cold. The 1 : 2 : 5 acid forms deliquescent needles. N. H. M.

Synthesis of Anhydrides of Aromatic Sulphinic Acids. By R. Otto and A. Milch (*Ber.*, **20**, 3337—3338).—In a previous paper (Abstr., 1885, 1231), Otto and Rössing showed that when an alkyl chlorocarbonate is allowed to act on an alkaline sulphinate, an alkyl sulphinate and carbonic anhydride are formed. The authors now find that a similar reaction takes place when carbonic oxychloride is substituted for the chlorocarbonate. Phosgene gas and sodium benzenesulphinate yield carbonic anhydride, sodium carbonate, and *benzenesulphinic anhydride*, $(C_6H_5SO)_2O$. This compound is soluble in ether, but is decomposed immediately by water and alcohol, forming the acid or the ethyl salt respectively. L. T. T.

Sulphoneketones. By R. and W. OTTO (*J. pr. Chem.* [2], **36**, 401—432).—Phenylsulphonacetone behaves as a ketone, forming with sodium hydrogen sulphite colourless, tabular crystals of a double salt; with hydroxylamine, mono- or tri-clinic needles of *phenylsulphonacetoxime*, $OH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}SO_2Ph$, melting at 147—148°; with ammonia, tabular crystals of *phenylsulphonacetonamine*,

$$NH{:}CMe{\cdot}CH_2SO_2Ph{\cdot}Me,$$

melting at 110—111°. With phenylhydrazine, it yields pale-yellow needles melting at 129°, of formula $N_2HPh{:}CMe{\cdot}CH_2{\cdot}SO_2Ph$, and with thiophenol it forms needles of *phenylsulphonacetone mercaptole*, $CMe(SPh)_2{\cdot}CH_2{\cdot}SO_2Ph$, melting at 103—104°. When oxidised, it yields acetic acid, benzenesulphonic acid, and carbonic anhydride. When reduced by hydrogen in an acid solution, phenyl mercaptan and isopropyl alcohol are formed; in an alkaline solution, benzenesulphinic acid and isopropyl alcohol. With bromine, it yields *phenylsulphonebromacetone*, crystallising in colourless, silky needles, soluble in hot alcohol, and melting at 96°, and *phenylsulphonedibromacetone*, also in colourless needles, melting at 113—114°. With potassium hydroxide, it yields potassium acetate and methylphenylsulphone.

Diphenylsulphonacetone has the symmetrical constitution $CO(CH_2{\cdot}SO_2Ph)_2$, for it is converted by potassium hydroxide into potassium phenylsulphonacetate and methylphenylsulphone. Diphenylsulphonacetoxime, $OH{\cdot}N{:}C(CH_2{\cdot}SO_2Ph)_2$, obtained by heating the above compound with hydroxylamine hydrochloride, crystallises in rectangular tables melting at 136—137°. The phenylhydrazine compound forms yellow needles melting at 171°. With thiophenol, *diphenylsulphone mercaptan* is formed as a fine lustrous, crystalline powder, insoluble in water, melting at 190—191°.

A triphenylsulphone-derivative was not obtained by acting on phenyldibromacetone with sodium benzenesulphinate.

Paratolylsulphonacetone, $COMe{\cdot}CH_2{\cdot}SO_2{\cdot}C_7H_7$, forms long, silky needles, soluble in alcohol, benzene, and chloroform, and melts at 51°. The bromo-derivative, $CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}SO_2{\cdot}C_7H_7$, crystallises in needles or rectangular plates, melts at 129—130°, and is sparingly soluble in hot water.

Diparatolylsulphonacetone, $CO(CH_2{\cdot}SO_2{\cdot}C_7H_7)_2$, forms white, rhombic tables melting at 152°, soluble in hot glacial acetic acid and in chloroform. Paratolylsulphonephenylsulphonacetone,

$$C_7H_7{\cdot}SO_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}SO_2Ph,$$

prepared by the action of paratolylsulphonebromacetone on sodium benzenesulphinate, crystallises in rhombic plates and melts at 112°.

Calcium phenylsulphonacetate crystallises with 2½ mols. H_2O in small needles, the lead salt with 2 mols. H_2O; the silver salt when heated yields methylphenylsulphone and not diphenylsulphonacetone as was expected.

A. G. B.

Ethereal Salts of Benzoic Sulphinide. By R. N. BRACKETT (*Amer. Chem. J.*, 9, 406—410).—The *methyl salt*, $C_6H_4{<}\substack{CO\\SO_2}{>}NMe$, is obtained from methyl iodide and the potassium or silver salt. It crystallises from alcohol or hot water in flat needles melting at 131—132°. The *ethyl salt*, $C_7H_4SO_3NEt$, melting at 96—97° (Fahlberg and List give 93—94°), is prepared in like manner; at the same time some ethyl orthosulphamine benzoate is formed. The propyl salt melts at 60—70°.

When benzoic sulphinide is treated with phosphorus pentachloride, and methyl alcohol added in the cold, a crystalline substance is precipitated, probably $C_6H_4<\substack{SO_2\\CCl_2}>NH$; when this is boiled with methyl alcohol, it dissolves, and the solution on cooling yields first crystals of an acid melting above 330°, and then crystals melting at 123—125°; the latter is the dimethyl ether, $C_6H_4<\substack{C(OMe)_2\\SO_2\text{——}}>NH$, of Remsen and Palmer, and when boiled with water and barium carbonate yields the barium salt of benzoic sulphinide. H. B.

Aromatic Lead Compounds. By A. POLIS (*Ber.*, **20**, 3331—3336).—The author has obtained lead tetraphenyl (Abstr., 1887, 572) in measurable crystals. These crystals are colourless prisms belonging to the tetragonal system; axial ratio $a : c = 1 : 0·3808$. The corresponding tin compound gives $a : c = 1 : 0·38935$. Silicon tetraphenyl gives $a : c = 1 : 0·43969$. The three compounds are isomorphous, the value of the principle axis decreasing with the increase of atomic weight of the grouping element. *Lead diphenyl dichloride*, $PbPh_2Cl_2$, is formed by the action of chlorine on a carbon bisulphide solution of lead tetraphenyl or from the nitrate (*loc. cit.*) by precipitation with potassium chloride. It is a white powder, insoluble in alcohol and ether, sparingly soluble in chloroform, benzene, and carbon bisulphide. The *oxide*, $PbPh_2O$, obtained by the action of soda on an aqueous solution of the nitrate, is a white powder which does not fuse without decomposition. It does not seem to form a hydroxide, but is strongly basic in character, and dissolves in acids to form salts. The *acetate*, $PbPh_2(OAc)_2 + 2H_2O$, forms long, colourless needles; the *formate*, $PbPh_2(CHO_2)_2 + H_2O$, colourless needles; the *basic cyanide*, $PbPh_2Cy·OH$, a white powder; the *thiocyanate*, $PbPh_2(CNS)_2$, and the *phosphate*, $(PbPh_2)_2P_2O_8$, white, flocculent precipitates; the *basic carbonate*, $(PbPh_2·OH)_2CO_3$, a white powder, and the *chromate*, $PbPh_2CrO_4$, a yellow precipitate which, when crystallised from a mixture of alcohol and benzene, yields yellowish crystals.
L. T. T.

Methylketole. By E. FISCHER (*Annalen*, **242**, 372—383).—Many of the compounds mentioned in this paper have been previously described by the author (Abstr., 1887, 265). *Benzylidenemethylketole*, $CHPh(C_9H_8N)_2$, begins to melt at 242°, and melts completely at 246—247°. In the crystalline state this substance is sparingly soluble in the ordinary solvents, with the exception of acetone. The amorphous precipitate which is formed when water is added to the solution in acetone is freely soluble in ether and alcohol, but it soon changes to the less soluble form. On oxidation, dimethylrosindole is produced (Abstr., 1887, 588).

Metanitrobenzaldehyde and methylketole readily unite, forming *metanitrobenzylidenemethylketole.* This substance is soluble in acetone, melts at 263°, and yields a red colouring matter on oxidation. When reduced with zinc-dust and ammonia it is converted into *metamidobenzylidenemethylketole*, $NH_2{\cdot}C_6H_4{\cdot}CH(C_9H_8N)_2$. This base is soluble in ether, alcohol, and benzene. The preparation of *ethylidenemethylketole*, $CHMe(C_9H_8N)_2$, from paraldehyde, zinc chloride, and methylketole has already been described (Abstr., 1887, 265). It melts at 191°, and boils with slight decomposition. It is freely soluble in alcohol, ether, and acetone.

By acting on methylketole and phthalic anhydride with zinc chloride at 100°, a compound of the composition $C_{17}H_{13}NO_3$ is obtained. It forms colourless prisms and dissolves in hot alcohol and acetic acid. The acid melts above 200°, and completely decomposes at a higher temperature. The author is of opinion that the acid may have the formula $C_9H_8N{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$.

In the presence of zinc chloride, 1′-methylindole and phthalic anhydride unite to form phthalylmethylindole, $C_{26}H_{20}N_2O_2$. The new compound crystallises in prisms, melts at 300°, and dissolves in hot acetone. W. C. W.

Azo- and Amido-derivatives of Methylketole. By P. WAGNER (*Annalen*, **242**, 383—388).—The preparation of methylketoleazobenzene, $C_8H_4N(Me)N_2Ph$, has been already described (Abstr., 1887, 265). The compound is soluble in alcohol, ether, and benzene. On reducing the alcoholic solution with tin and hydrochloric acid, aniline and amidomethylketole are formed. The ketole crystallises in plates and melts at 112—113°. It is soluble in alcohol, ether, chloroform, and light petroleum. The hydrochloride crystallises in prisms, which turn pink on exposure to the air. When reduced with zinc-dust and hydrochloric acid, amidomethylketole yields first methylketole and then hydromethylketole. On oxidation with ferric chloride, amidomethylketole yields a mixture of two compounds, one of which is very soluble in alcohol. The other is less soluble in alcohol, crystallises in plates, and has the empirical formula C_9H_7NO. It melts at 225° with partial decomposition.

When dry hydrogen iodide is passed into an ethereal solution of methylketole, an amorphous precipitate (C_9H_9N,HI) is produced. The compound is decomposed by water into its two components.

W. C. W.

Derivatives of β-Naphthindole. By A. STECHE (*Annalen*, **242**, 367—371).—*β-Naphthylhydrazinelevulinic acid* is deposited as a crystalline precipitate on the addition of water to an alcoholic solution of levulinic acid and β-naphthylhydrazine in their molecular proportions. At 170°, the acid is converted into the *anhydride.* This substance melts at 119°, and is deposited from hot alcohol in needle-shaped crystals. *Ethyl naphthylhydrazinelevulinate* is formed by the direct union of ethyl levulinate with β-naphthylhydrazine. It is crystalline, and melts at 129—130°. It is converted into methyl-β-

naphthindolacetic acid, $C_{10}H_6<\substack{NH\\CMe}>C\cdot COOH$, by the action of zinc chloride at 130—135°. This acid is freely soluble in alcohol, ether, acetone, and acetic acid. The silver salt is decomposed by boiling in water, forming a metallic mirror.

The acid decomposes at 210°, yielding carbonic anhydride and *dimethyl-β-naphthindole*, $C_{12}NH_7Me_2$ [$Me_2 = 2'' : 3''$]. The latter compound melts at 126° and dissolves freely in alcohol and acetic acid. It yields a dark-red picrate and a crystalline nitrosamine, and gives a characteristic blue coloration with acetic acid and ferric chloride. On reduction with zinc-dust and hydrochloric acid, *hydrodimethyl-β-naphthindole* is produced. This base is an oily liquid, which turns red on oxidation. The platinochloride is crystalline and is decomposed by boiling water. W. C. W.

Hydroxydiphenyl Bases. By A. WEINBERG (*Ber.*, **20**, 3171—3178).—*Diamidohydroxydiphenylsulphonic acid*,

$$OH\cdot C_{12}H_6(NH_2)_2\cdot SO_3H\ [OH : NH_2 : SO_3H : NH_2 = 3 : 4 : 6 : 4'],$$

is prepared by reducing with stannous chloride, at a temperature not exceeding 30°, 300 grams of sodium benzene-azoparaphenolsulphonate dissolved in 500 c.c. of water. After 12 hours, the product is treated with hydrogen sulphide, filtered and evaporated to a small bulk; the *hydrochloride* of the sulphonic acid separates in large, clear crystals. The free sulphonic acid crystallises in needles from water, which dissolves it readily.

Diamidohydroxydiphenyl, $C_{12}H_7(NH_2)_2\cdot OH$ [$= 4' : 4 : 3$], is formed when diamidohydroxydiphenylsulphonic acid hydrochloride is heated with water at 180°. It crystallises in colourless plates melting at 185°, and is almost insoluble in water, readily soluble in dilute caustic alkali solutions. The alkaline solutions oxidise quickly when exposed to air. The hydrochloride is very readily soluble.

Diamidohydroxyphenyltolylsulphonic acid, $OH\cdot C_{12}H_5Me(NH_2)_2\cdot SO_3H$ [$NH_2 : Me : OH : NH_2 : SO_3H = 4' : 3' : 3 : 4 : 6$], is prepared from the dye obtained from orthotoluidine and paraphenolsulphonic acid. It crystallises in colourless needles which decompose when heated. It dissolves sparingly in water, readily in acids and alkalis.

Diamidohydroxyphenyltolyl, $NH_2\cdot C_6H_3Me\cdot C_6H_3(NH_2)\cdot OH$, prepared by heating the sulphonic acid with water at 180°, crystallises from water in lustrous plates melting at 177°; it dissolves readily in dilute aqueous potash, sparingly in ether and benzene. The *sulphate* is almost insoluble in water, more soluble in dilute acid.

Diamido-ethoxydiphenylsulphonic acid, $C_{12}H_{16}N_2SO_4$, is obtained by reducing sodium benzene-azophenetoïlsulphonate. It crystallises in needles sparingly soluble in cold water. The *hydrochloride* (with 2 mols. H_2O) is readily soluble.

Diamido-ethoxydiphenyl, $C_{14}H_{12}O(NH_2)_2$, is prepared by heating the above sulphonic acid with water at 170° for 8 to 10 hours; it forms flat, lustrous needles which melt at 134—135°, dissolves sparingly in water, ether, and benzene, readily in alcohol. When heated with hydrochloric acid, diamidohydroxydiphenyl (m. p. 185°) is formed.

The *sulphate* crystallises in prisms, sparingly soluble in water, readily in hydrochloric acid.

Diamido-ethoxyphenyltolylsulphonic acid is sparingly soluble in water. The *hydrochloride* forms large, prismatic crystals (with 4 mols. H_2O). The *barium salt* (with 8 mols. H_2O) crystallises in concentrically grouped needles.

Diamido-ethoxyphenyltolyl, $C_{15}H_{18}N_2O$, crystallises from water in flat needles melting at 117·5°; it is sparingly soluble in water, cold alcohol, ether and benzene. When saponified, it yields diamidohydroxyphenyltolyl melting at 177°.

Diamido-ethoxynaphthylphenyl, $NH_2·C_6H_4·C_{10}H_5(OEt)·NH_2$

$$[NH_2 : C_{12}H_{12}NO = 1 : 4; \quad C_6H_4·NH_2 : OEt : NH_2 = 1 : 3 : 4],$$

is prepared by dissolving benzene-azo-β-naphthol in the equivalent amount of alcoholic potash, adding ethyl bromide, and boiling the whole for 24 hours under a slight pressure. When cold, it is filtered and evaporated down, when the benzene-azo-β-naphthylethyl oxide remains as a dark-red oil. This is reduced with stannous chloride. The diamide melts at 72°, dissolves readily in alcohol, ether, and benzene; the alcoholic solution shows a greenish-blue, the ether and benzene solutions a violet fluorescence. The normal *sulphate* is sparingly soluble in water; the *hydrochloride* crystallises in needles of a silky lustre. N. H. M.

Dinitrobenzidine. By E. v. BANDROWSKI (*Monatsh.*, **8**, 471—474).—By the hydrolysis of dinitrodiphthalylparabenzidine with sulphuric acid at 130°, two *dinitrobenzidines* are produced together with phthalic acid. One modification less soluble in ammonia, forms long needles melting at 218—221°, and decomposing, when heated, with explosion. The more soluble modification forms saffron-yellow needles melting at 196—197°; it is also distinguished from its isomeride by its greater solubility in alcohol and dilute acids. A dinitrobenzidine has previously been described by Strakosch, who obtained it by the nitration of acetylbenzidine; this has been shown by Brunner and Witt to be an ortho-derivative. From its method of formation, it would seem that this compound is identical with the isomeride melting at 218—221° described above, although Strakosch assigns a melting point of over 300° to the substance. However, the identity of the two substances is confirmed by the formation from both of them of the same tetramidodiphenyl. V. H. V.

Bases produced by Nascent Formaldehyde. By J. TRÖGER (*J. pr. Chem.* [2], **36**, 225—245).—A crystalline, monacid base, probably $CH_2(CH:N·C_6H_4Me)_2$, is produced by the action of nascent formaldehyde on paratoluidine; it melts at 134°, dissolves in alcohol, ether, &c., but is insoluble in water; it forms a crystalline hydrochloride, sulphate, platinochloride, and picrate. When treated with nitrous acid, carbonic anhydride and nitric oxide are evolved, and a compound having the formula $C_{16}H_{16}N_4O_2$ is formed; this substance dissolves in acetic acid, but is insoluble in alcohol, ether, water and concentrated hydrochloric acid; it melts at 260—264° with decomposition, gives Liebermann's reaction, and also the nitric acid reaction with ferrous sulphate. A very similar product is obtained when the base is treated with nitric acid, nitrogen dioxide and carbonic anhydride being evolved; with acetic anhydride, it yields a very stable compound, $C_{42}H_{46}N_4O_5$.

Nascent formaldehyde and dimethylaniline yield tetramethyldiamidodiphenylmethane, from which a crystalline picrate and nitro-derivative, $CH_2[C_6H(NO_2)_3{\cdot}NMe_2]_2$, were prepared.

Tetramethyldiamidodiphenylethane, $C_2H_4{\cdot}(C_6H_4{\cdot}NMe_2)_2$, is produced when dimethylaniline and carbon bisulphide are treated in alcoholic solution with zinc-dust and concentrated hydrochloric acid; it is a colourless, crystalline compound, melts at 87°, dissolves in ordinary solvents, but is insoluble in water; combines with methyl iodide, forms a crystalline picrate (melting at 190°) and platinochloride, and with nitric acid yields dinitronitrosodimethylaniline,

$NO{\cdot}C_6H_2(NO_2)_2{\cdot}NMe_2$. F. S. K.

Condensation Products from Paratoluidine and Paranitrobenzaldehyde. By A. Bischler (*Ber.*, **20**, 3302—3306).—When paranitrobenzaldehyde, paratoluidine and concentrated hydrochloric acid are heated together in alcoholic solution, *α-paranitrophenyldiparamidotolylmethane*, $NO_2{\cdot}C_6H_4{\cdot}CH(C_6H_3Me{\cdot}NH_2)_2$, is formed. Crystallised from benzene, this substance forms white needles of the formula $3C_{21}H_{21}N_3O_2 + C_6H_6$, which lose their benzene at 110—120° and melt at 170—172°. It is but sparingly soluble in alcohol and ether, easily in boiling benzene. Its salts crystallise with difficulty, and are decomposed by water. The *platinochloride*, $C_{21}H_{21}N_3O_2,H_2PtCl_6$, forms yellow crystals soluble in boiling alcohol.

When, however, paranitrobenzaldehyde and paratoluidine are heated with strong sulphuric acid, an isomeric compound, *β-paranitrophenyldiparamidotolylmethane*, is formed. It crystallises in yellow scales melting at 126—127°, and is easily soluble in cold benzene and boiling alcohol or ether. It also is but a feeble base, but its salts are more easily crystallisable than those of the α-compound. The *hydrochloride* forms yellow needles, the *platinochloride* yellow scales.

The author believes the isomerism of these two compounds to be due to the benzaldehyde nucleus displacing ortho-hydrogen atoms in the toluidine in the α-case, meta-atoms in the β- (sulphuric acid) condensation. L. T. T.

Compounds of Ketones with Dimethylaniline and Diethylaniline. By O. Döbner and G. Petschow (*Annalen*, **242**, 333—348).—The formation of tetramethyldiamidodiphenylpropane by the action of zinc chloride on acetone (1 mol.) and dimethylaniline (2 mols.), has been already described by Döbner (Abstr., 1879, 787). By a similar reaction, *tetrethyldiamidodiphenylpropane*, $CMe_2(C_6H_4{\cdot}NEt_2)_2$, has been prepared from diethylaniline and acetone. The base forms silky needles and melts at 76°. It is soluble in ether, carbon bisulphide, benzene, and light petroleum. The salts are very soluble and crystallise with difficulty. The *hydriodide*, $C_{23}H_{34}N_2,2HI$, forms pale-yellow plates, freely soluble in alcohol and in hot water.

Tetramethyldiamidotriphenylmethane is the chief product of the action of zinc chloride on acetophenone and dimethylaniline. Tetramethyldiamidodiphenylmethane and triphenylbenzene are also formed.

Tetramethyldiamidotriphenylethane, $CMePh(C_6H_4{\cdot}NMe_2)_2$, is a pale-yellow oil, which gradually acquires a dark-red colour on exposure to the air. It boils above 360° with partial decomposition; under reduced pressure it may be distilled without undergoing any change. It is non-volatile in steam, and dissolves freely in ether, benzene, light petroleum and warm alcohol. The salts are very soluble in water and do not crystallise. It yields amorphous precipitates with the chlorides of gold, platinum, and mercury.

An acetic acid solution of the base turns blue on the addition of lead or manganese peroxide.

Benzophenone and dimethylaniline yield dimethylamidotriphenylmethane. Methyl hexyl ketone and dimethylaniline yield tetramethyldiamidodiphenylmethane and a liquid base, $C_{14}H_{23}N$, which is probably a hexyldimethylaniline. The chief product of the action of zinc chloride on diethyl ketone and dimethylaniline is tetramethyldiamidodiphenylmethane.
W. C. W.

Derivatives of Triphenylmethane. By C. Ullmann (*J. pr. Chem.* [2], **36**, 246—272).—Diamido-derivatives of triphenylmethane are produced by the action of benzaldehyde on a mixture of a suitable aromatic base, and its hydrochloride. Aniline yields diamidotriphenylmethane; orthotoludine gives *diamidorthotolylphenylmethane*, a white, microcrystalline powder whose melting point could not be determined.

Paratoluidine yields *diamidoparatolylphenylmethane* which crystallises from a mixture of benzene and light petroleum with ½ mol. C_6H_6, in concentric groups of yellow needles and melts at 185—186°; it is a diacid amine, and forms a hydrochloride, picrate, &c. The colourless, crystalline *acetyl-derivative*, $C_{21}H_{18}(NHAc)_2$, melts at 217—218°; the *benzoyl-derivative*, $C_{21}H_{18}(NHBz)_2$, melts at 196°. By means of the diazo-reaction, diamidoparatolylphenylmethane can be converted into the di-iodo-derivative $C_{21}H_{18}I_2$, crystallising in brownish-red prisms and melting at 167—168°. When distilled with zinc-dust, it yields paratoluidine and methylacridine, and, therefore, probably has the constitution $CHPh(C_6H_3Me{\cdot}NH_2)_2$ [Me : CH : NH_2 = 1 : 3 : 4]; from its formation by the above method, and as it can also be obtained by Mazzara's and by O. Fischer's methods, it follows that it is not necessary that the para-position with respect to the amido-group should be free in order to synthesise amidotriphenylmethane-derivatives.

In the preparation of the para-compound, a substance of the formula $C_{21}H_{18}N_2$ is also formed; it crystallises in long, nearly colourless needles, melts at 177—178°, and gives an orange-yellow, crystalline platinochloride.
F. S. K.

Tetramethyldiamidothiobenzophenone. By O. BAITHER (*Ber.*, **20**, 3289—3298).—The author is inclined to think that this substance, which he previously described (Abstr., 1887, 816), is really a thioketone, and identical with the compound obtained by Fehrmann (this vol., p. 156) from auramine. He believes the differences of properties and melting points are due to want of purity and difficulty in exactly determining the melting point. He now gives the melting point as 193—194°.

When the ketone is heated with benzoic chloride in carbon bisulphide solution, a *dichloro-derivative*, $CCl_2(C_6H_4{\cdot}NMe_2)_2$, is formed, which is soluble in alcohol and glacial acetic acids, sparingly so in benzene and chloroform, and when heated decomposes. With water, it yields Michler's ketone, $CO(C_6H_4{\cdot}NMe_2)_2$, and is probably the compound prepared from the latter in the manufacture of auramine colouring matters.

With benzoic chloride, the thioketone forms an *additive derivative*, $CS(C_6H_4{\cdot}NMe_2)_2,COPhCl$. This substance is crystalline and melts below 200°, but was not obtained quite pure. It is soluble in acetic acid and in benzene. Alcohol and chloroform also dissolve it, but at the same time decompose it into its two constituents. Acetic chloride yields a similar derivative, $CS(C_6H_4{\cdot}NMe_2)_2,COMeCl$, which is crystalline and begins to decompose at 160°. It is soluble in alcohol, acetic acid, chloroform, and benzene.

When the thioketone is heated with acetic anhydride and sodium acetate, it yields a compound, $C_{38}H_{46}N_4O_4S$, of which the constitution is probably $S[C(C_6H_4{\cdot}NMe_2)_2{\cdot}OAc]_2$. It forms a green powder which begins to decompose at 120°.

When heated with aniline, the thioketone appears to yield chiefly Michler's ketone, but with aniline hydrochloride it yields phenylauramine. The author found the melting point of the latter to be 170—171°. Phenylhydrazine appears to convert the thioketone into the corresponding oxy- (Michler's) ketone.

In his previous communication, the author described the product of the action of nitric acid on the thioketone as trinitrodimethylaniline. He now finds, however, that it is the same compound,

$$CO[C_6H_2(NO_2)_2{\cdot}NMe{\cdot}NO_2]_2,$$

obtained from Michler's ketone. With hydroxylamine, this compound yields van Romburgh's compound, $CO[C_6H_2(NO_2)_2{\cdot}NHMe]_2$. It is probable that an oxime is first formed and is subsequently decomposed.

L. T. T.

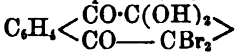
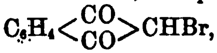
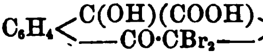
Ring-formation with Elimination of Hydrogen Bromide or Nitrous Acid. By E. LELLMANN and O. SCHMIDT (*Ber.*, **20**, 3154—3157).—When β-naphthylamine is treated with glycerol, orthonitrophenol, and sulphuric acid, it yields β-naphthaquinoline in which the condensation has occurred at the 1 : 2 position; it was thought that by starting from α-bromo-β-naphthylamine, in which the 1 position is occupied, the condensation would occur at the 2 : 3 positions. α-Bromo-β-naphthylamine [$Br : NH_2 = 1 : 2$] was obtained by brominating β-acetonaphthalide; it was then treated with glycerol, orthonitrophenol, and sulphuric acid, and the product of the reaction crystallised from light petroleum; it melted at 93·5°, and on examination it was found that β-naphthaquinoline had been formed with elimination of hydrogen bromide. α-Nitro-β-naphthylamine when treated in a similar manner yields the same compound with elimination of nitrous acid. The conclusion drawn is that the β′-carbon-atom is far less prone to ring-formation than the α-carbon-atom. The nitrophenol takes no part in the reaction, the result being the same whether it is present or not. F. S. K.

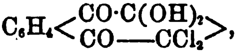
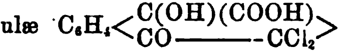
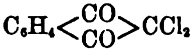
Isomeric Naphthylaminesulphonic Acids. By G. SCHULTZ (*Ber.*, **20**, 3158—3162).—Bayer and Duisberg (this vol., p. 732) have stated that when β-naphthylamine is sulphonated, a mixture of sulpho-acids is obtained from which a hitherto unknown β-naphthylamine-δ-monosulphonic acid can be isolated; this compound yields a β-naphthol-δ-sulphonic acid which is identical with Casella and Co.'s naphtholsulphonic acid F; conversely, by heating this acid with ammonia, Bayer and Duisberg obtained a compound identical with β-naphthylamine-δ-sulphonic acid. Weinberg and Lange (this vol., p. 160) throw doubt on the identity of the acid which they themselves obtained from naphtholsulphonic acid F and that prepared by Bayer and Duisberg from β-naphthylamine. The author concludes that Weinberg obtained an impure product only, and gives proofs of the identity of the acids in question. F. S. K.

Intramolecular Migration in β-Naphthylaminesulphonic Acids. By A. WEINBERG (*Ber.*, **20**, 3353—3355).—When β-napthylamine-α- and γ-sulphonic acids are added to sulphuric acid (3 parts) previously heated at 160°, and the whole kept at this temperature for 1½ hours, they both yield as chief product the 2 : 2′ acid together with the 2 : 3′ acid. The same product is formed by sulphonating β-naphthylamine sulphate. It is possible that Bayer and Duisberg's δ-acid (Abstr., 1887, 732) really consisted of this mixture. (Compare Schultz, preceding Abstract.) N. H. M.

Conversion of Naphthylaminesulphonic Acid into Dichloronaphthalene. By H. ERDMANN (*Ber.*, **20**, 3185—3187).—When Witt's naphthalenedisulphonic acid (Abstr., 1886, 554) is diazotised, the product warmed with phosphorus pentachloride, and then distilled, dichloronaphthalene [1 : 4′] melting at 107° is obtained, together with some α-monochloronaphthalene. The yield of dichloronaphthalene is 30 to 40 per cent. of the theoretical. N. H. M.

Action of Bromine on Diamido-α-naphthol. By T. ZINCKE and C. GERLAND (*Ber.*, **20**, 3216—3231; compare Abstr., 1887, 838). —When bromine acts on bromamido-α-naphthaquinonimide or bromohydroxynaphthaquinonimide, the main products are the tribromide, $C_{10}H_6Br_3NO_3$, and the dibromide, $C_9H_4Br_2O_2$; the latter melts at 176°, which is rather higher than the figure given by Kronfeld. In the second case, a small quantity of a third bromide melting at 130° is also formed.

By the bromination of bromamidonaphthaquinone or of bromohydroxynaphthaquinone, four brominated compounds are obtained, of which three are formed in very small quantity. Two of these are not yet worked out, the other is identified as the dibromide $C_9H_4Br_2O_2$. The main product is a dibromo-compound, $C_{10}H_6Br_2O_4$, *dibromotriketohydronaphthalene hydrate*,  $C_6H_4<\begin{array}{l}CO\cdot C(OH)_2\\CO—CBr_2\end{array}>$; this crystallises in matted needles, melts at 114—115° with decomposition, is readily soluble in alcohol, chloroform, and benzene, less readily in light petroleum, and is soluble in alkalis with yellow coloration. It is readily converted into bromoxy-α-naphthaquinone and hypobromous acid, either when heated alone or when boiled with benzene, toluene, dilute alcohol, or dilute acetic acid. When boiled with water, carbonic anhydride is evolved and a mixture of bromoxynaphthaquinone and the dibromide $C_9H_4Br_2O_2$ separates. When dissolved in ethyl or methyl alcohol and treated with hydrogen chloride, chlorohydroxy-α-naphthaquinone is formed. When boiled with aqueous potash, it yields a monobromo-compound, crystallising in small, nearly colourless plates and needles, and melting at 118—119°, and probably of the constitution $C_6H_4<\begin{array}{l}C(OH)\\CO\end{array}>CBr$ or  $C_6H_4<\begin{array}{l}CO\\CO\end{array}>CHBr$, probably due to the decomposition of an acid,  $C_6H_4<\begin{array}{l}C(OH)(COOH)\\CO\cdot CBr_2\end{array}>$, first formed, and for whose existence some evidence is adduced.

The corresponding dichloro-compound,  $C_6H_4<\begin{array}{l}CO\cdot C(OH)_2\\CO—CCl_2\end{array}>$, prepared in similar manner, crystallises in thick, white needles, melts at 105° without decomposition, and is far more stable than the dibromo-compound. When treated with alkalis, it is converted into a crystalline compound melting at 128—129°, and if the alkaline solution is oxidised, small lustrous plates melting at 124—125°. The authors regard these substances as having the formulæ  $C_6H_4<\begin{array}{l}C(OH)(COOH)\\CO———CCl_2\end{array}>$ and  $C_6H_4<\begin{array}{l}CO\\CO\end{array}>CCl_2$ respectively.

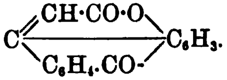
A chlorobromo-compound, $C_{10}H_6ClBrO_4$, was also prepared; it is less stable than the dichloro-compound, crystallises in white needles, melts at 104—105°, and when oxidised in alkaline solution yields plates of a substance melting at 141°.

When the dibromide $C_9H_4Br_2O_4$ is treated with aqueous soda, it yields bromoform, phthalic acid, and the monobromo-compound $C_9H_5BrO_2$ described above. A. J. G.

Synthesis of Anthracoumarins from Cinnamic and Metahydroxybenzoic Acids. By S. v. KOSTANECKI (*Ber.*, **20**, 3137—3145). When a mixture of cinnamic acid and metahydroxybenzoic acid, or any hydroxy-derivative of the latter, is heated with concentrated sulphuric acid, condensation products are formed.

From metahydroxybenzoic acid, *anthracoumarin*, $C_{16}H_8O_3$, is obtained as a yellow, crystalline compound melting at 260°; it dissolves readily in hot glacial acetic acid, benzene, concentrated sulphuric acid, and hot baryta-water, sparingly in alcohol; with boiling alkalis, it forms a yellow solution of green fluorescence which probably contains a salt of the corresponding coumaric acid. It is not dissolved by alkalis in the cold, whilst the compounds obtained from dihydroxybenzoic or gallic acid are readily soluble.

This fact shows that the hydroxyl-group has taken part in the condensation, and from the great similarity between these compounds and anthraquinone-derivatives the constitution of anthracoumarin is probably



$$C\begin{matrix}\diagup CH\cdot CO\cdot O\diagdown \\ \diagdown C_6H_4.CO\diagup\end{matrix}C_6H_3.$$

In like manner *metahydroxyanthracoumarin*, $C_{16}H_8O_4$, is obtained from symmetrical dihydroxybenzoic acid. By sublimation or crystallisation from acetic acid, yellow needles are formed which melt at 325° and are only sparingly soluble in any ordinary solvent; they dissolve, however, in alkalis and sulphuric acid. When boiled with baryta-water, the coumarin-ring is probably split, an insoluble barium salt being precipitated. The yellow crystalline *monacetyl*-derivative, $C_{16}H_7O_4Ac$, melts at 255°.

Orthodihydroxyanthracoumarin, $C_{16}H_8O_5$, has already been obtained by Jacobsen and Julius (this vol., p. 56), who gave to it the name "styrogallol;" this compound and also its diacetyl-derivative were prepared, the latter melts at 260°, and its formation lends support to the constitution assigned to the anthracoumarins. Orthodihydroxyanthracoumarin can be fixed by a mordant, a fact which is in accordance with a theory put forward by the author (see this vol., p. 274).

F. S. K.

Purpurogallin. By S. C. Hooker (*Ber.*, **20**, 3259—3260).—The author recommends the following method of preparing purpurogallin:—20 grams of pyrogallol is dissolved in 330 c.c. of cold water and treated with a solution of 87 grams of potassium ferricyanide in 330 c.c. of water. Gas is evolved, the solution loses its deep red colour, and purpurogallin separates; in about ½ hour the oxidation is complete. The yield is 13 to 14 per cent. of the pyrogallol employed.

Purpurogallin is formed in the oxidation of an aqueous solution of gallic acid by sodium nitrite.

Purpurogallin dissolved in sulphuric acid gives an intense, but fugitive, violet coloration when a trace of nitrous acid or a nitrite is added. The reaction is very characteristic and delicate.

A. J. G.

Hydrogenation of Aromatic Hydrocarbons. By E. Bamberger and W. Lodter (*Ber.*, **20**, 3073—3078).—The hydrocarbons are boiled with amyl alcohol and sodium, the whole poured into water, and the upper layer dried with sodium carbonate and distilled. The yield varies with different hydrocarbons from 50 to 80 per cent. of the theoretical.

Tetrahydroretene, $C_{18}H_{22}$, forms a clear viscous oil which when kept from air remains liquid; in open vessels it solidifies, probably becoming oxidised to retene. It boils at 280° under 50 mm. pressure.

Tetrahydro-acenaphthene, $C_{12}H_{14}$, is a clear, colourless, viscous oil of a slightly aromatic odour, boiling at 249·5° (corr.) under 719 mm. pressure.

Tetrahydrodiphenyl, $C_{12}H_{14}$, is a clear, colourless, viscous oil having a slight odour of diphenyl. It boils at 244·8° under 716 mm. pressure.

Dihydronaphthalene, dihydroanthracene (m. p. 108·5°), and tetrahydrophenanthrene were also prepared. N. H. M.

Sulphocamphylic Acid. By A. DAMSKY (*Ber.*, **20**, 2959—2967). —When ammonium sulphocamphylate is distilled with ammonium chloride, a yellowish-brown oil of peculiar turpentine-like odour is obtained, which, on fractionation, can be separated into two portions, one boiling at 108—110° and the second at 195—196°. These were separately examined.

The fraction boiling at 108—110° is a colourless, mobile liquid, having the odour of the crude product, and a sp. gr. = 0·7949 at 11·5°. It has the composition C_8H_{14}, and is a non-aromatic hydrocarbon, possibly identical with that obtained by Moitessier by distilling copper camphorate (*Jahresb.*, 1866, 410). On treatment with concentrated nitric acid, it is violently attacked and completely resinified, but when dissolved in acetic acid and treated with an acetic acid solution of nitric acid, no action occurs. Oxidation with chromic acid mixture does not convert it into an aromatic acid, and with permanganate it yields only oily fatty acids; whilst, contrary to the behaviour of aromatic hydrocarbons, it does not form an acid amide on treatment with amidoformic chloride. Bromine reacts with it readily, yielding an unstable, crystalline compound, $C_8H_{12}Br_2$, and subsequently liquid higher substitution-products, whilst the unstable, crystalline additive-compounds, C_8H_{14},HCl and C_8H_{14},HBr, are formed when it is treated with hydrogen chloride and hydrogen bromide respectively.

The fraction boiling at 195—196° undergoes slight decomposition at each distillation, and is a colourless liquid, having an odour similar to that of the lower fraction. It has probably the composition $C_{10}H_{14}O$, and forms oily compounds with hydroxylamine hydrochloride and phenylhydrazine hydrochloride; the *oxime* having probably the formula $C_{10}H_{14}\colon N\cdot OH$.

When potassium sulphocamphylate is fused with twice its weight of potassium hydroxide and the melt extracted with ether, a brown, resinous mass is obtained, which, on distillation in a vacuum, yields a pale-yellow, readily crystallisable oil. The crystals have the composition $C_9H_{12}O_2$, are readily soluble in alcohol and ether, very sparingly soluble in hot water and melt at 99°. The compound, although prepared by Kachler's method (Abstr., 1874, 154), and having the same composition, differs from the substance prepared by him in its lower melting point and marked acid character. The *silver* salt, $C_9H_{11}O_2Ag$, is soluble in hot water; the *calcium* salt, $(C_9H_{11}O_2)_2Ca + 2H_2O$, forms yellowish crystals, soluble in hot water; the *barium* salt, $(C_9H_{11}O_2)_2Ba + 2H_2O$, is crystalline and soluble in hot water; the *methyl* salt was also prepared and is crystalline. Treated with bromine, the acid yields a crystalline compound with the evolution of hydrogen bromide, and it is not reduced by the action of sodium amalgam. When distilled with soda-lime, it yields a yellow oil, which on rectification forms a colourless, mobile liquid of the composition C_8H_{12}, boiling at 133—135°, and polymerising on exposure to the air. W. P. W.

Action of Sulphuric Acid on Terebenthene. By J. BOUCHARDAT and J. LAFONT (*Compt. rend.*, **105**, 1177 — 1179). — The product of the gradual action of 467 grams of sulphuric acid on 9340 grams of French terebenthene boiling at 155—157° (rotatory power −32·2°) was distilled in a current of steam; 79 grams of sulphuric acid remained in the free state, the rest having formed a compound $2C_{10}H_{16},H_2SO_4$, which is almost though not quite fixed. This compound could not be isolated from the colophene with which it is mixed. It is a neutral substance and does not combine with potassium hydroxide. Alcoholic potash is without action in the cold, but at 150° decomposition takes place with formation of volatile products and the compound $C_{10}H_{16},SO_2KH$, which crystallises from its aqueous solution in thin lamellæ.

The portion of the original product which distils with steam consists mainly of the unaltered hydrocarbon, without any camphene. The fraction boiling at 175—180° has the composition $C_{10}H_{16}$, oxidises very readily, and is somewhat lighter than the original terebenthene. It absorbs hydrogen chloride readily yielding a liquid product, and when the latter is distilled in a vacuum, it yields cymene and terpilene hydrochloride, $C_{10}H_{16},2HCl$, melting at 48°. The rotatory power of the corresponding terpilene is only one-fifth or one-sixth that of another terpilene obtained from the same terebenthene by a different method.

The fraction boiling below 165° was treated successively four times with sulphuric acid, always with a similar result, but the fraction boiling at 157°, which gradually became smaller and smaller in quantity, diminished in rotatory power, and after a fifth treatment was converted into an easily solidified camphene. This camphene is formed by the decomposition of the small quantity of the sulphur compound which distils over with the water. This fraction, in fact, always contains a small quantity of free sulphuric acid.

When the original product, which is not volatile in steam, is heated at 200—250°, an energetic reaction takes place, water, sulphurous anhydride, and sulphur being produced. The liquid products contain a slightly active lævogyrate compound boiling at 156°, cymene, terpilene, and dextrogyrate camphenols. C. H. B.

Pimaric Acids. By A. VESTERBERG (*Ber.*, **20**, 3248—3253).—In a previous paper (Abstr., 1886, 1038) the author showed that the mother-liquor from the preparation of dextropimaric acid contained β-pimaric acid. From the very vigorous lævorotatory power of this acid, the name lævopimaric acid is now given to it; its separation and purification were attended with great difficulty. *Lævopimaric acid*, $C_{20}H_{30}O_2$, isomeric with dextropimaric acid, crystallises in the rhombic system; axial ratios, $a : b : c = 0·81042 : 1 : 0·61407$; observed faces: ∞P, $\infty \breve{P} \infty$, $P/2$, $2\breve{P}\infty$, $0P$. It melts between 140° and 150°, and is insoluble in water, readily soluble in all the other usual solvents, its solubility being greater than that of the dextro-acid. One part of the acid dissolves in 10·8 parts of 98 per cent. alcohol at 15°. A solution of 3·174 parts of lævopimaric acid in 100 c.c. of alcohol has a lævorotatory power $[\alpha]_D = -272°$. It forms readily crystallisable salts, of which the sodium, ammonium, and lead salts are described.

The author considers it very probable that Calliot's pyromaric acid (this Journal, 1874, 457) is a mixture of dextro- and lævo-pimaric acids. A. J. G.

Action of Phenylhydrazine on Santonin. By C. GRASSI (*Chem. Centr.*, 1887, 1163—1164; from *Rend. R. Acc. Lincei* [4], 3, 521—522).—When a solution of santonin (10 grams) is heated with phenylhydrazine (10 grams) in acetic acid solution (sp. gr. 1·06), a yellow *hydrazide*, $C_{15}H_{18}O_2{\cdot}N_2HPh$, separates, which melts at 220°, and is not decomposed by acids. Hydrochloric acid dissolves it in the cold with a reddish-yellow colour; on heating, a scarlet precipitate is formed. The hydrazine compound yields a platinochloride. J. W. L.

Lakmoïd and Litmin. By W. N. HARTLEY (*Proc. R. Dublin Soc.*, 5, 159).—Lakmoïd (Abstr., 1885, 148) is soluble in strong alcohol, insoluble in water. A solution in 50 per cent. alcohol retains its colour with but slight alteration for several months. Litmin is insoluble in strong alcohol, but soluble in spirit of 50 per cent.; the solution was bleached after a time although not exposed to bright light. The photographic spectra of the two substances did not differ markedly. From these results, it follows that the two substances are not identical. Lakmoïd is a better reagent than litmin. A. J. G.

New Brazilin-derivative. By C. SCHALL and C. DRALLE (*Ber.*, 20, 3365—3366).—*Tetramethylbrazileïn*, $C_{16}H_{10}O_5Me_4$, is prepared by mixing 2·7 grams of brazilin with 0·8 gram of sodium (each dissolved in alcohol); 8 grams of methyl iodide is then added, and the whole warmed on a water-bath until the colour changes to a yellowish-brown. The greater portion of the alcohol is distilled off and the rest evaporated on a water-bath. It is washed with water, dissolved in ether, and washed with dilute aqueous soda. It forms a brittle, transparent, amber-coloured mass which becomes crystalline when ether is poured over it. When crystallised from alcohol, it is obtained in colourless crystals melting at 138—139°. The compound has the properties of a phenol alkyl ether; it does not change when exposed to air, and yields an additive product with ammonia. N. H. M.

Metanitroquinoline. By A. CLAUS and A. STIEBEL (*Ber.*, 20, 3095—3097).—*Metanitroquinoline*, $C_9NH_6{\cdot}NO_2$, is prepared from 10 grams of nitraniline, 2·6 grams of picric acid, 14 grams of glycerol, and 14 grams of sulphuric acid. The mixture is afterwards boiled for some hours. The product after being freed from resin, is treated with light petroleum to remove the phenanthroline, which is also formed in the reaction, and recrystallised from alcohol or water. It forms long, thin, colourless needles, melting at 131·5° (uncorr.). The *hydrochloride* crystallises in long, yellowish-white needles, melts at 225° with evolution of gas, and decomposes in contact with water. The *nitrate* crystallises in long, flat needles of a satiny lustre, not very readily soluble in water. The *platinochloride* forms large, amber-coloured prismatic crystals. *Metamidoquinoline*, $C_9NH_6{\cdot}NH_2$, prepared by reducing the nitro-compound with stannous chloride, forms long, hair-like, yellowish needles which melt at 186° (uncorr.); it is readily soluble in ether, chloroform, &c. When heated, it yields a sublimate of splendid red needles. It does not distil with steam. (Compare Abstr., 1887, 810). N. H. M.

Constitution of Quinoline-derivatives. By J. FREYDL (*Monatsh.*, 8, 580—583).—The so-called β-amidoquinoline on conversion into the corresponding diazochloride and treatment of the same with potassium cyanide, yields a cyanoquinoline identical with the metacyanoquinoline of Bedall and Fischer. On hydrolysis, this nitrile yields a quinolinecarboxylic acid, identical with that obtained from an amidobenzoic acid by Skraup's reaction. The amidoquinoline is also converted by the diazo-reaction into a chloroquinoline, identical with the compound obtained by La Coste (Abstr., 1886, 159) from metachloraniline by Skraup's reaction. Then in the above group the substituted groupings are in the 2 position as derived from the 1 : 3 benzenoïd derivatives. V. H. V.

Sulphonation of Quinoline. By G. v. GEORGIEVICS (*Monatsh.*, 8, 577—579).—By the sulphonation of quinoline with Nordhausen acid, La Coste, as also Bedall and O. Fischer, obtained a mixture of the 1 : 2 and 1 : 3 quinolinesulphonic acids, the proportion of each which is formed being dependent on the conditions of the experiment. It is here shown that if the sulphonation is effected with ordinary sulphuric acid, the 1 : 4 sulphonic acid is produced, a result confirmed by the conversion of the acid into the corresponding nitrile and carboxylic acid. V. H. V.

Quinoline. By E. LELLMANN and G. LANGE (*Ber.*, **20**, 3084—3089; compare Abstr., 1887, 737).—Calcium parabromobenzenesulphonate crystallises is well-formed, monoclinic crystals with 2 mols. H_2O: $a : b : c = 0{\cdot}5872 : 1 : 0{\cdot}5168$; $\beta = 85° \; 14' \; 42''$ (compare Goslich, this Journal, 1876, i, 929). Parabromometamidobenzenesulphonic acid crystallises in well-formed prisms with 1 mol. H_2O (not 1½ mol. H_2O, Goslich, *loc. cit.*).

Orthobromoquinoline-anasulphonic acid, $C_9NH_5Br{\cdot}SO_3H$ [$Br : SO_3H = 1 : 4$], is prepared by heating 5 grams of parabromometamidobenzenesulphonic acid, 6 to 7 grams of orthonitrophenol, 20 grams of glycerol, and 25 to 27 grams of sulphuric acid in a reflux apparatus at 155—160° for six hours. The product is treated with water, steam-distilled, treated with baryta, filtered, and the filtrate boiled with animal charcoal. By precipitating the barium as exactly as possible with sulphuric acid and carefully evaporating the filtrate, the sulphonic acid is obtained in small, lustrous plates with 1 mol. H_2O. The *calcium salt* with 6½ mols. H_2O crystallises in long needles, readily soluble in water.

Tetrahydroquinoline-anasulphonic acid, $C_9NH_{10}\cdot SO_3H + H_2O$, is formed when 5 grams of bromoquinolinesulphonic acid is heated on a water-bath with concentrated hydrochloric acid and tin. It crystallises from dilute solutions in rhombic crystals; $a : b : c = 0{\cdot}5041 : 1 : 0{\cdot}7511$, and from concentrated solutions is monoclinic crystals; $a : b : c = 0{\cdot}4855 : 1 : 0{\cdot}5298$; $\beta = 55° 10'$. When treated with oxidising agents, it shows the reactions characteristic of tetrahydroquinoline-derivatives.

The quinolinesulphonic acid previously prepared (*loc. cit.*) from metamidobenzenesulphonic acid, also yields a tetrahydroquinolinesulphonic acid which completely resembles that just described.

N. H. M.

β-Quinolinedisulphonic Acid. By W. La Coste and F. Valeur (*Ber.*, **20**, 3199—3201).—β-Quinolinedisulphonic acid, prepared by heating the pure barium salt with the necessary amount of sulphuric acid, crystallises in slender white needles, readily soluble in water, insoluble in alcohol, ether, benzene, and chloroform. (Compare Abstr., 1887, 379.) The barium salt is obtained by treating the potassium salt with barium acetate. The potassium salt (with 1 mol. H_2O), is insoluble in alcohol, readily soluble in boiling water. When this salt is fused with 3 parts of potash at 160°, potassium β-hydroxyquinolinesulphonate is formed. *β-Hydroxyquinolinesulphonic acid* crystallises in yellow, lustrous plates, melting at 270—275°; it dissolves readily in hot water, sparingly in alcohol, and still less in chloroform and carbon bisulphide.

β-Dihydroxyquinoline, $C_9NH_4(OH)_2$, is prepared in a manner similar to the α-compound (Abstr., 1886, 629), except that the temperature is only raised to 250—255°. It crystallises in slightly brown needles, readily soluble in ether, alcohol, benzene, chloroform, and carbon bisulphide, insoluble in water. It melts at 68°, and sublimes at a higher temperature in slender white needles. The salts are stable, but difficult to crystallise. (Compare also Abstr., 1887, 973.)

N. H. M.

Tetrahydroquinaldine. By M. Möller (*Annalen*, **242**, 313—321).—Tetrahydroquinaldine has already been described by Jackson (Abstr., 1881, 742), and by Döbner and Miller (Abstr., 1884, 183). The nitronitroso-compound, $NO_2\cdot C_{10}NH_{11}\cdot NO$, crystallises in golden plates, and melts at 152°. Methylhydroquinaldine, $C_{10}H_{12}NMe$, has been prepared by Döbner and Miller (*loc. cit.*). It can also be prepared by the action of tin and hydrochloric acid on quinaldine methiodide. *Methylhydroquinaldine methiodide*, $C_{10}NH_{12}Me,MeI$, crystallises in needles, melts at 205°, and dissolves freely in water and in hot alcohol. Freshly precipitated silver oxide converts it into the ammonium base, $C_{10}NH_{12}Me,MeOH$, a crystalline, hygroscopic compound. The aurochloride crystallises in lemon-coloured needles, and the dichromate in six-sided plates. The platinochloride forms brick-red crystals, soluble in hot water. The base is decomposed by heat, yielding methyl, alcohol, and methyltetrahydroquinaldine

Ethyltetrahydroquinaldine, $C_{10}NH_{12}Et$, is a colourless liquid, boiling at 256°. The platinochloride and methiodide are crystalline. The latter melts at 187° and dissolves in water, but is not acted on by a solution of potassium hydroxide. W. C. W.

Quinaldine Alkyl Iodides. By M. Möller (*Annalen*, **242**, 300—312).—Quinaldine methiodide and methylquinaldinium hydroxide have been previously described by Döbner (Abstr., 1884, 184), and by Bernthsen and Hess (Abstr., 1885, 558) respectively. In addition to the salts prepared by Bernthsen and Hess, the ammonium base yields an aurochloride, $C_{10}H_9NMeCl,AuCl_3$, and a dichromate,

$$(C_{10}NH_9Me)_2Cr_2O_7,$$

crystallising in lemon-coloured needles. The dichromate detonates at 90°. Ethylquinaldinium hydroxide on exposure to the air changes into a carmine-coloured resin. The platinochloride, $(C_{10}NH_9Et)_2PtCl_6$, is deposited from hot water in ruby prisms. The aurochloride,

$$C_{10}NH_9EtCl,AuCl_3,$$

forms golden needles. The dichromate detonates at 100°. *Quinaldinepropiodide* forms greenish-yellow prisms, soluble in water and in hot alcohol. It melts at 166—167°. The ammonium base is amorphous. It is soluble in alcohol and ether. The platinochloride, aurochloride, and dichromate are crystalline. *Quinaldine butiodide* is prepared by heating quinaldine with isobutyl iodide at 115° in molecule proportion. It crystallises in plates, and melts at 172°. The amyl iodide requires a temperature of 140—145° for its formation. It is crystalline, soluble in water and hot alcohol, and melts at 175°.

Orthomethylquinaldine methiodide is deposited from alcohol in yellow needles, and melts at 221°. The ammonium base is tolerably stable, and does not change rapidly on exposure to the air. The platinochloride, dichromate, and aurochloride are crystalline. The base is decomposed by heat, yielding orthomethylquinaldine. *Orthomethylquinaldine ethiodide* is deposited from alcohol in yellow needles, and melts at 228°. The ammonium base is a stable, oily liquid, and it forms crystalline platino- and auro-chlorides.

Paramethylquinaldine unites with methyl iodide at the ordinary temperature. The compound melts at 236—237°, and dissolves freely in water. The ammonium base is unstable. The platinochloride, dichromate, and aurochloride crystallise in needles.

W. C. W.

Conversion of Indoles into Hydroquinolines. By E. Fischer and A. Steche (*Annalen*, **242**, 348—366).—In previous communications (Abstr., 1887, 588 and 976), the authors have described the conversion of methylketole into dimethyldihydroquinoline and dimethyltetrahydroquinoline, which are derivatives of β-methylquinoline. In the preparation of dimethyldihydroquinoline, a monomethyldihydroquinoline is formed as a bye-product. Dihydroethyldimethylquinoline and ethylmethylketole have already been described by the authors (*loc. cit.*).

Ethylmethyldihydroquinoline [Et : Me = 1′ : 3′], prepared by the action of methyl iodide on ethylmethylketole and methyl alcohol at 120°, is a colourless oil which turns pink on exposure to the air. It boils at 254—255°, and forms salts which are freely soluble in alcohol and water. With ferric and platinic chlorides, it yields crystalline precipitates.

Trimethyldihydroquinoline, $C_9NH_6Me_3$ [1′ : 3′ : 4′], boils at 244°. The hydriodide crystallises in long prisms. The sulphate is precipitated from its alcoholic solution in crystalline scales on the addition of ether. The platinochloride is decomposed by boiling water.

The dimethyldihydro-β-naphthaquinoline, previously described by the authors (*loc. cit.*), is an imide base. The hydriodide and platinochloride are sparingly soluble in alcohol and in water.

The methiodides of the quinolines and dihydroquinolines are easily decomposed by alkalis, but the methiodides of the tetrahydroquinolines are not attacked.

Dihydroquinolines containing methylene in the indole-ring turn red on exposure to the air. W. C. W.

α-Alkylcinchonic Acids and α-Alkylquinolines. By O. Döbner (*Annalen*, **242**, 265—290).—The preparation of the α-alkylcinchonic acids and the properties of some of these compounds have already been described by the author (Abstr., 1887, 504). In the preparation of α-isopropylcinchonic acid, a neutral substance of the composition $C_{19}H_{20}N_2O$ is obtained as a bye-product. It is insoluble in alkalis. α-Isopropylcinchonic acid, $C_9NH_5Pr^{\beta}\cdot COOH$ [2′ : 4′], crystallises with 1½ mols. H_2O. The hydrochloride, $C_{13}H_{13}NO_2,HCl$, forms colourless plates, freely soluble in water. The platinochloride, which is abnormal $(C_{13}H_{13}NO_2,HCl)_4,PtCl_4 + H_2O$, and the aurochloride, $(C_{13}H_{13}NO_2)_2,HAuCl_4$, are crystalline. α-Isopropylquinoline picrate is deposited from alcoholic solutions in yellow plates. It melts at 150°. The platinochloride crystallises with 2 mols. H_2O.

A neutral substance of the composition $C_{20}H_{22}N_2O$ is formed by the action of aniline on an ethereal solution of pyruvic acid and isovaleraldehyde. It crystallises from alcohol in silky needles, and melts at 160°. If a warm alcoholic solution is substituted for the ethereal solution, α-isobutylcinchonic acid is produced. The acid crystallises with 1½ mols. H_2O. The hydrochloride, $C_{14}H_{15}NO_2,HCl + H_2O$, crystallises in colourless plates, and dissolves freely in water. The platinochloride, $(C_{14}H_{15}NO_2)_2,H_2PtCl_6$, is also crystalline. α-Isobutylquinoline picrate crystallises in plates, soluble in alcohol. It melts 161°.

On mixing together cold alcoholic or ethereal solutions of furfuraldehyde, pyruvic acid, and aniline, a neutral substance of the composition $C_{20}H_{16}N_2O_2$ is formed, but with warm alcoholic solutions, *α-furfurcinchonic acid*, $(C_4H_3OC_9NH_5)\cdot COOH$, is produced. This acid crystallises in greenish-yellow needles. It melts with decomposition between 210° and 215°, and dissolves freely in alcohol, ether, benzene, and in hot water. The silver, lead, and copper salts are sparingly soluble in water. The hydrochloride, nitrate, and sulphate are freely soluble. The platinochloride, $(C_{14}H_9NO_3)_2,H_2PtCl_6$, and the aurochloride, $(C_{14}H_9NO_3)_2,AuCl_3$, crystallise in needles. *α-Furfurquinoline* is obtained by heating furfurcinchonic acid at 300°. It melts at 92°, and boils above 300°. It crystallises in thick needles, and dissolves in alcohol, ether, and benzene. The platinochloride, $(C_{13}H_9NO)_2,H_2PtCl_6 + 2H_2O$, and the aurochloride,

$$C_{13}H_9NO,HAuCl_4,$$

crystallise in needles, and dissolve in hot water. The dichromate forms orange-red needles. It is soluble in hot water. The dry salt decomposes at 100°. The picrate melts at 186°, and is deposited from hot alcohol in large yellow plates. W. C. W.

α-Phenylcinchonic Acid and its Homologues. By O. Döbner and M. Gieseke (*Annalen*, **242**, 290—300).—On mixing together ethereal solutions of aniline, pyruvic acid, and benzaldehyde, a compound of the composition $C_{22}H_{18}N_2O$ is obtained in the form of a crystalline mass, insoluble in acids, alkalis, and water. It melts at 225°, and dissolves freely in ether, benzene, acetic acid, and light petroleum. Strong acids and hot alkalis decompose the compound, yielding aniline and resinous products.

The preparation and properties of α-phenylcinchonic acid have been previously described by the authors (Abstr., 1887, 504). The silver, lead, copper, and zinc salts were obtained in the form of amorphous precipitates.

A compound of the composition $C_{24}H_{22}N_2O$ is deposited in crystals on mixing ethereal solutions of paratoluidine, pyruvic acid, and benzaldehyde. It melts at 204—205°, and is insoluble in acids and alkalis. If warm alcoholic solutions are used, only a small quantity of this compound is formed, the chief product being *paramethyl-α-phenylcinchonic acid*,

$$C_9NH_4MePh{\cdot}COOH\ [Me : Ph : COOH = 3 : 2' : 4'].$$

This acid is deposited from alcohol in yellow needles. It melts at 228°, and is soluble in alcohol and ether. The platinochloride,

$$(C_{17}H_{13}NO_2)_2,H_2PtCl_6,$$

forms golden needles. On distillation with soda-lime, paramethylphenylcinchonic acid yields paramethyl-α-phenylquinoline. *Orthomethyl-α-phenylcinchonic acid*, [1 : 2′ : 4′], melts at 245°, and is freely soluble in ether and hot alcohol. The silver salt, $C_{17}H_{12}NO_2Ag + H_2O$, crystallises from hot water in needles. On distillation with lime, the acid yields *orthomethyl-α-phenylquinoline*. The base boils above 360°, and melts at 49—50°. W. C. W.

Parabenzoylquinaldine and Paradiquinaldine. By E. Hinz (*Annalen*, **242**, 321—329).—Paraldehyde acts on parabenzoylaniline dissolved in hydrochloric acid, forming *parabenzoylquinaldine*, C_9NH_5MeBz, and several bye-products. The new base melts at 67—68°, boils above 300°, and dissolves freely in hot water, alcohol, ether, benzene, chloroform, and light petroleum. The platinochloride,

$$(C_{17}H_{13}NO)_2,H_2PtCl_6 + 2H_2O,$$

crystallises in needles, and is sparingly soluble in water. The anhydrous salt melts at 108—110°. The dichromate also crystallises in needles. The methiodide melts at 220°.

Diquinaldine is prepared by the action of paraldehyde on benzidine dissolved in hydrochloric acid. The yield is poor. Diquinaldine, $C_{20}H_{16}N_2$, melts at 206—207°, and dissolves in alcohol, benzene, chloroform, and acetone. It boils with slight decomposition above 360°.

The *platinochloride*, $C_{20}H_{16}N_2,H_2PtCl_6 + 2H_2O$, is sparingly soluble in hot water. The nitrate, $C_{20}H_{16}N_2,2HNO_3$, crystallises in needles, and is soluble in water. The dichromate is crystalline.

W. C. W.

Quinoline. By E. Bamberger (*Ber.*, **20**, 3338—3344).—*Quinolinephenacyl bromide*, $COPh\cdot CH_2\cdot C_9NH_7Br$, is prepared by mixing equal mol. weights of quinoline and bromacetophenone dissolved in ether or in benzene; it separates in tufts of white needles. The yield is quantitative. It dissolves readily in alcohol and water, sparingly in ether and benzene, begins to decompose at 115—118°, and melts at about 165°. The *zincochloride* crystallises from water in small, thick, strongly refractive prisms; the nitrate crystallises in clear, strongly refractive prisms of a vitreous lustre, which are generally bent. The physiological action of the nitrate on mice, frogs, and cats is described; it resembles that of curare. When a quinolinephenacyl salt is treated with alkalis, the ammonium base is obtained together with a scarlet dye; the *base* forms white flakes, readily soluble in ether.

Formylphenacylanthranilic acid, $COOH\cdot C_6H_4\cdot N(CH_2\cdot COPh)\cdot COH$, is formed when 16 grams of potassium permanganate dissolved in 600 c.c. of water is gradually added to a cooled solution of 10 grams of quinolinephenacyl bromide in 1200 c.c. of water; after 12 hours, the colourless liquid is filtered, the manganese peroxide extracted several times with boiling water, and the collected filtrates from 50 grams of the phenacyl bromide evaporated down to 2 to 2·5 litres. It is then made acid, left for 24 hours in a cool place, and the crystals thus obtained are recrystallised from much water. It crystallises from dilute alcohol in white plates of a satiny lustre, melting at 184°, readily soluble in alcohol, less in hot water. Benzoic acid is formed as the chief product of the reaction. When the acid is boiled with dilute sulphuric acid, formic acid is obtained.

Pyridinephenacyl bromide, $C_5NH_5Br\cdot CH_2\cdot COPh$, prepared from pyridine and bromacetophenone, crystallises from a mixture of ether and alcohol in slender, lustrous, strongly refractive prisms. The *chromate* crystallises from water in lustrous, orange-coloured prisms; the *zincochloride* separates from its hot aqueous solution in lustrous, rhombic plates. When the bromide is treated with aqueous soda, it is decomposed into pyridine and benzoic acid.

N. H. M.

Acetic Tripiperide. By J. BUSZ and A. KEKULÉ (*Ber.*, **20**, 3246—3248).—Ortho-amides, corresponding with the ortho-salts formed by acetic and other acids, have not yet been prepared. Experiments made with primary amines and with secondary amines of the type NHR'_2, have failed to yield such compounds, but with secondary amines of the type NHR'', of which piperidine is an example, success was attained.

Acetic tripiperide, $CMe(C_5NH_{10})_3$, is obtained by heating acetic trichloride (α-trichloroethane) for 4 to 5 hours in a reflux apparatus. It boils at 133—134° under 15 mm., or 261—263° under ordinary pressure. It is very stable, yielding but slight quantities of acetic acid when boiled for days with water or dilute acetic acid. The hydrochloride is crystalline and insoluble in ether; the platinochloride crystallises in golden-yellow plates.

Chloroform acts very slowly on piperidine, yielding a base boiling at 98°, which seems to be *orthoformic piperide*, $CH(C_5NH_{10})_3,H_2O$.

Benzotrichloride reacts readily with piperidine, but whether a benzoic tripiperidide is formed is not yet established. A. J. G.

Oxidation Products of Papaverine. By G. GOLDSCHMIEDT (*Monatsh.*, **8**, 510—528).—In continuation of former experiments on the oxidation of papaverine by potassium permanganate (Abstr., 1886, 479), the author has more fully examined dimethoxycinchonic acid and other products formed. Papaverine hydrochloride yields oxalic, hemipinic, and veratric acids, which are contained in the filtrate from the reduced manganese peroxide; on treatment of this last with sulphurous acid, and extraction of the residue with hydrochloric acid, papaveraldine hydrochloride and dimethoxycinchonic acid are obtained, together with a substance of the formula $C_{10}H_9NO_4$. This last, named *hemipinisoimide*, to distinguish it from the isomeric hemipinimide obtained by Liebermann by the action of hydroxylamine on opianic acid, forms small, white needles melting above 300°; it dissolves only on prolonged heating with alkali, but is at the same time decomposed into ammonia and hemipinic acid. It is also distinguished from hemipinimide by the unstable character of its potassium-derivative. The formula of this substance is discussed, but without satisfactory conclusions.

Dimethoxycinchonic acid, $C_9NH_4(OMe)_2\cdot COOH$, crystallises with $2H_2O$ in small needles; it melts at 205° with violent evolution of carbonic anhydride, and formation of dimethoxyquinoline; it gives a brownish-red turbidity with ferric chloride, but no reaction with ferrous sulphate. Solutions of its salts give gelatinous precipitates with barium, calcium, copper, and silver salts. The *hydrochloride* crystallises with 2 mols. H_2O in glistening needles, and the *platinochloride* in groups of yellow needles. By hydriodic acid, the dimethoxy-acid is converted into *dihydroxycinchonic* acid, $C_9NH_4(OH)_2\cdot COOH$, which is an amorphous powder, melting at 221° with violent evolution of gas. It gives a violet coloration with ferric chloride, and a reddish-yellow with ferrous sulphate. Its salts are all of a yellow colour, thus resembling those of hydroxycinchonic acid obtained by Weidel from the corresponding sulphonic acid.

Dimethoxyquinoline, $C_9NH_5(OMe)_2$, obtained by heating the dimethoxycinchonic acid, as also from papaveraldine when it is heated with alkali, forms a *hydrochloride* crystallising with $3H_2O$, a *picrate* crystallising in citron-yellow needles, and a *chromate* in small, orange-yellow, rhombic crystals.

This dimethoxyquinoline from papaverine is isomeric with that obtained from veratric acid; a list is given of the points of difference between the salts of these two bases. It is probable that in the methoxyquinoline from veratric acid, the methoxy-groups are in the position 1 : 2, but in that from papaverine the groups are in the positions 2 : 3; the author proposes to confirm this view by further experiments. V. H. V.

Adenine. By A. KOSSEL (*Ber.*, **20**, 3356—3358; compare Abstr., 1886, 556).—*Adenine nitrate*, $C_5H_5N_5,HNO_3 + \frac{1}{2}H_2O$, crystallises in stellate groups of needles; the dry salt dissolves in 110·6 parts of water. The *hydrochloride* (with ½ mol. H_2O) forms transparent, monoclinic crystals, $a : b : c = 2·0794 : 1 : 1·8127$; $\beta = 61° 40'$; the anhydrous salt dissolves in 41·9 parts of water. The *platinochloride*, $(C_5H_5N_5)_2,H_2PtCl_6$, crystallises from its dilute solution in needles; when a concentrated solution is boiled long, the *salt*,

$$C_5H_5N_5,HCl,PtCl_4,$$

separates as a bright yellow powder. The *silver compound*, $C_5H_4N_5Ag$, is obtained as an amorphous powder by adding an ammoniacal silver solution to a hot ammoniacal solution of adenine; with a large excess of silver solution, the *compound* $C_5H_5N_5,Ag_2O$ is formed. The *acetyl-derivative*, $C_5H_4N_5Ac$, crystallises in small, white plates, readily soluble in hot water and alcohol, soluble in dilute acids and alkalis; it does not melt at 260°. The *benzoyl-derivative*, $C_5H_4N_5Bz$, forms long, thin, lustrous needles, melting at 234—235°, readily soluble in hot alcohol, soluble in dilute acids and in ammonia.

Adenine is very stable towards acids, alkalis, and oxidising agents, but is readily reduced by zinc and hydrochloric acid, behaving like hypoxanthine. N. H. M.

Ptomaïnes and Leucomaïnes. By A. GAUTIER (*Bull. Soc. Chim.*, **48**, 6—23).—A summary of our present knowledge concerning ptomaïnes, giving an account of the results obtained by the author, Brieger, and others, whose papers have from time to time appeared in Abstracts in this Journal (see Abstracts, 1881, 100, 224; 1882, 1115; 1884, 89, 188; 1885, 676; 1886, 634; also *Bull. de l'Acad de Med.*, 1886). C. H. B.

Empirical Formula of Cholic Acid. By P. LATSCHINOFF (*Ber.*, **20**, 3274—3283).—Mylius has lately (Abstr., 1887, 982) upheld Strecker's formula $C_{24}H_{40}O_5$ for cholic acid, against this formula $C_{25}H_{42}O_5$ proposed by the author. The latter has therefore carefully re-examined this acid and its derivatives, with the result of confirming the formula $C_{25}H_{42}O_5$. He has been unable to obtain the acid perfectly anhydrous. Cholic acid crystallises in two forms (i) in tetrahydric crystals, and (ii) in prismatic crystals. The first, obtained by crystallisation from alcohol, acetone, ether (of which it requires 510 parts at 18° for solution), isobutyl alcohol, or ethyl acetate, has the formula $C_{25}H_{42}O_5 + \frac{1}{4}H_2O$. It only loses this water of crystallisation at or above 145°, and partial decomposition always takes place simultaneously. Fusion ultimately results at 160—180°. The prismatic crystals, obtained by the precipitation of an acetic solution of the acid with water, have the formula $C_{25}H_{42}O_5 + H_2O$. They lose $\frac{3}{4}$ mol. H_2O at 120°, but the remaining $\frac{1}{4}$ is only lost at or above 145°. The author believes Mylius to have taken the not fully dehydrated acid as anhydrous. When this acid is dissolved in phenol, it forms white prisms, which give analytical results, agreeing with the formula $C_{25}H_{42}O_5 + \frac{1}{8}H_2O + \frac{7}{8}C_6H_6O$. It seems that the last trace of water is very firmly united to the cholic acid, and that when crystallised from other media with which it unites, the acid only takes up the complementary quantity of the medium. Thus the crystals from an alcoholic solution had the formula $C_{25}H_{42}O_5 + \frac{1}{8}H_2O + \frac{7}{8}C_2H_6O$.

Attempts to obtain mineral salts of the acid showed that here also a similar state of things existed. The salts all contained an excess of the base, that excess being, as in the case of the water of crystallisation, about one-eighth of an equivalent. With aniline and toluidine, however, cholic acid yields well-defined crystalline salts, which give numbers agreeing with those required by theory. *Aniline cholate*, $C_{25}H_{42}O_5,NH_2Ph$, forms needles melting at 140°; *metatoluidine cholate* needles melting at 140—180°. L. T. T.

Action of Sodium Chloride in Dissolving Fibrin. By J. R. Green (*J. Physiol.*, 8, 372—377).—When fibrin is extracted with a 5 or 10 per cent. solution of sodium chloride, a proteïd goes into solution; on renewing this solution daily, removing that added on the previous day, it is found that in 32 to 35 days the whole of the fibrin is dissolved. In all these experiments, there was perfect freedom from putrefaction. When dissolved in this way, the fibrin is decomposed, with the formation of two globulins, one of which coagulates at 56°, is soluble in 1 per cent. sodium chloride solution, is readily converted into syntonin and alkali-albumin, and is not precipitated by weak acid; the other is insoluble in 1 per cent. sodium chloride solution, but soluble in a 10 per cent. solution; it coagulates on heating at 59—60°, is readily converted into alkali-albumin, but not into syntonin, the acid added for the latter purpose precipitating it, and in suspension it is not acted on. In some of its reactions, the former substance recals the behaviour of fibrinogen, but neither corresponds with fibrinogen or serum globulin, and the latter cannot be made to re-form fibrin. W. D. H.

Hæmatoporphyrin. By C. A. MacMunn (*J. Physiol.*, 8, 384—389).—A brownish pigment is scattered over several superficial portions of the mollusc *Solecurtus strigillatus*. On microscopical examination, it is found that, in the foot especially, the pigment is situated at the border of the cells, so that the boundaries between them are marked much in the same way that endothelium cells are demonstrated by the use of silver nitrate. Granules in the cells contain the same pigment. Spectroscopic examination shows that the pigment is hæmatoporphyrin; this is identical with Moseley's polyperythrin (*Quart. J. Mic. Science*, **17**, 1); the bands are identical with those seen in the pigment from the dorsal streak of the earthworm; a list of 12 other invertebrates in which the same pigment has been found is given. In many of these there is no hæmoglobin present, but the universal distribution of the histohæmatins, and the fact that these yield some of the decomposition products of hæmoglobin, fully explain the occasional appearance of a hæmoglobin-derivative in invertebrate animals (see Abstr., 1886, 638). W. D. H.

Physiological Chemistry.

Influence of Sleep on the Activity of Respiratory Combustion. By L. DE SAINT-MARTIN (*Compt. rend.*, **105**, 1124—1128).—Experiments with doves show that, independently of the effect produced by fasting, natural sleep reduces the quantity of carbonic anhydride exhaled by about one-fifth, and reduces the quantity of oxygen absorbed by about one-tenth.

Experiments with dogs show that during sleep produced by morphine the proportion of carbonic anhydride exhaled falls to one-half the normal amount; during sleep produced by chloral or chloroform it falls to one-third the normal proportion.

When anæsthesia by chloroform is sufficiently long continued the blood becomes impoverished in oxygen and is charged with an amount of carbonic anhydride very considerably in excess of the normal proportion. In the early stage of insensibility, there is a diminution in the proportion of carbonic anhydride in the blood, but this is due to secondary causes. C. H. B.

Coagulation of Fibrin and Intravascular Clotting. By F. KRÜGER (*Zeit. Biol*, **24**, 189—225).—Wooldridge has shown that the phenomenon of coagulation is brought about by a substance which he calls A fibrinogen, obtainable from peptone plasma by simply cooling, and that the cellular elements which were hitherto considered essential, although they may assist coagulation, are nevertheless of secondary import. In his Croonian lecture he described coagulation as essentially similar to crystallisation. In plasma there are three constituents concerned in coagulation—A, B, and C fibrinogen. A and B fibrinogen are compounds of lecithin and proteïd, and fibrin results from the transference of the lecithin from A fibrinogen to B fibrinogen. From this point of view the ferment is of secondary importance.

Wooldridge further found that a compound of lecithin and proteïd closely allied to the A fibrinogen, which he considers probably the precursor of A fibrinogen, exists in the testis and thymus gland of the calf, in the fluid of the lymph glands and the stromata of red blood-corpuscles. This compound is capable of causing widespread intravascular clotting in the entire absence of any cellular elements.

It is with reference to this last statement that the author joins issue. A large number of experiments have led him to the opposite conclusion, namely, that the corpuscular elements play the chief part in the coagulation, both within and without the body. He corroborates Wooldridge's statement, however, that the stromata of red blood corpuscles produce intravascular clotting.

The leucocytes obtained by centrifugalising the fluid of the lymph glands produce intravascular clotting, but the supernatant liquid, the author states, is inert, or almost so. He considers that any slight action of the fluid may be accounted for by the presence of some leucocytes, for he found it impossible to remove them completely, even by centrifugal action. J. P. L.

Influence of Calcium Sulphate on the Coagulation of the Blood. By J. R. Green (*J. Physiol.*, 8, 354—371).—A saline extract of washed blood clot contains fibrin ferment (Buchanan). Heating such an extract nearly to the boiling point delays the action of the ferment but does not destroy it; the ash was found to contain a definite and fairly constant amount of calcium sulphate. A saturated solution of calcium sulphate was prepared, and on adding 1 c.c. of this to 10 c.c. of diluted magnesium sulphate plasma, coagulation set in with great rapidity; a very small amount of the salt (0·001 per cent.) has considerable clotting power; this increases with the quantity of calcium sulphate used, but not proportionately. In other experiments with peptone or leech extract, in which coagulation was retarded by cold, the addition of calcium sulphate caused it to take place in some cases very rapidly, in others more slowly.

Calcium sulphate cannot be regarded as the fibrin ferment however; addition of that salt to pericardial fluid or to a sodium chloride solution of fibrinogen causes no coagulation in those fluids; but when the ferment is present, addition of salt accelerates the coagulation.

The next point investigated was whether it is possible to have coagulation in the absence of calcium sulphate; peptone-plasma was dialysed for three days into a 0·6 per cent. solution of sodium chloride; if water had been used outside the membrane, the globulins of the plasma would have been precipitated. Dilution of the plasma with saline solutions then caused no clotting, nor did the passing of a stream of carbonic anhydride through the plasma coagulate it as it does ordinary peptone-plasma. But on adding a little calcium sulphate to the diluted plasma coagulation rapidly set in.

In plasma prevented from coagulating by cold, or by admixture with magnesium sulphate, similar experiments were performed, dialysis being carried out at the temperature of 1°. After a week's dialysis, dilution caused no coagulation, but after adding calcium sulphate clotting set in, though slowly. It was suggested that the fibrin ferment exists as a zymogen in plasma, and is converted into ferment by the action of calcium sulphate. Horse's blood kept from clotting by cold was precipitated by a large excess of alcohol; after remaining for some weeks under the spirit, the precipitate was collected, dried, and extracted with a 0·6 per cent. sodium chloride solution; this was warmed with calcium sulphate for an hour, and then that salt removed by dialysis; but on diluting plasma or pericardial fluid with this there was no hastening of the coagulation; that is, there was no evidence of zymogen conversion.

Calcium sulphate helps the working of the ferment, but it is not concerned with its liberation. Quantitative experiments on the relation of the amount of fibrin formed to the amount of calcium sulphate added negative the idea that fibrin is a union of fibrin with that salt. Hammarsten (Maly's *Jahrsbericht*, **4**, 135) has shown that calcium phosphate is necessary for the proper activity of the rennet ferment.

W. D. H.

Secretion of the Gall Bladder. By B. Birch and H. Spong (*J. Physiol.*, 8, 378—383).—The fluid was obtained from two women in which a fistula remained in each case after the operation of cholecystotomy had been performed. A celluloïd cannula was found to be the best to use, as it did not set up the irritation consequent on the use of metallic ones. About 20 c.c. in the day was collected, but it is supposed that a third or more of the fluid was lost. In both cases the bile channels were completely closed off from the gall bladder, and no biliary constituents were present. The fluid was therefore the secretion of the mucous membrane of the gall bladder, and in both cases it had identical composition and properties. Both patients were also in excellent health. The fluid was sometimes clear, sometimes faintly opalescent; it was viscid; its specific gravity varied from 1·011 to 1·012 at 12·5°. On microscopic examination, it was found to contain a few leucocytes. It was always distinctly alkaline, which reaction must be attributed to alkaline sodium phosphate. The following is the approximate quantitative analysis in parts per 1000:—

Water and gases	979·7
Solids	20·3
A. Organic—	
Mucin Proteïd matter, a trace	12·09
B. Inorganic—	
Chlorine	3·84
Carbonic anhydride	0·29
Sodium (combined with Cl)	2·50
Soda (combined with CO_2)	0·41
Potassium salts and phosphates by difference	1·17
	20·30

The fluid has distinct diastatic properties, which were destroyed by boiling; the fermentation agent was not definitely separated; the alcoholic precipitate, however, was found to contain it, whilst none remained in the filtrate; the ferment was also non-diffusible. Some was filtered through a porous cell; the filtrate was inoperative on starch, whilst the residue, which evidently represented the mucin that could not get through the filter, was still active. The fluid had no curdling action on milk, and no emulsion was formed when it was mixed with cod-liver oil. The secretion, moreover, does not readily putrefy, although it was demonstrated by means of experiments with sterilised peptone infusion that it has no active power in restraining putrefaction; its apparent immunity from change being due to its poverty in nourishing material. The secretion cannot be regarded as playing any important part in digestion, the small diastatic action it possesses being shared by many fluids in the economy on which it does not confer any special digestive value. Its use is no doubt confined to lubricating the walls of the gall bladder, and it adventitiously adds some mucus to the bile which comes to repose in it. W. D. H.

Analyses of American Fishes. By W. O. ATWATER (*Amer. Chem. J.*, 9, 421—452).—52 species of American fishes were examined. The methods of analysis are described, and tables are given containing proportion of edible portion and the amounts of nitrogen, proteïds, ether extract, and ash of this portion of the fish. The composition varies very considerably, thus—

	Water.	Dry substance.	Albuminoïd.	Fat.	Ash.
Mackerel	73·4	26·6	18·3	7·1	1·3
Haddock	81·7	18·3	16·8	0·25	1·2
Cod	82·6	17·4	15·8	0·4	1·2
Halibut	75·4	24·6	18·4	5·2	1·1
Salmon	63·6	36·4	21·6	13·4	1·4
Spent salmon, female	78·2	21·8	17·8	2·8	1·2

H. B.

Ferments in Normal Urine. By E. STADELMANN (*Zeit. Biol.*, **24**, 226—260).—Very divergent opinions have from time to time been expressed with reference to the presence of ferments in normal urine. It may be safely said that all observers are agreed on the constant occurrence of pepsin in normal urine, but the most conflicting evidence is forthcoming as to the presence of trypsin.

Grützner and his pupils, Sahli, Gehrig, and Holovtschiner state that trypsin is a constant concomitant of normal urine, and that it is present in regular quantity. Mya and Belfanti state that both pepsin and trypsin are present in normal and pathological urine, except in cases of acute and chronic nephritis.

In opposition to this, Leo denies the occurrence of trypsin in all cases, but admits the presence of pepsin in normal and in most pathological cases. In cancer of the stomach and typhoid fever, pepsin, is however, absent.

In the present investigation, a complete survey of the whole subject has been undertaken. The occurrence of pepsin is further corroborated, but in no instance has trypsin been found. The author, therefore, considers with Leo that the apparent digestion of raw fibrin in alkaline urine, in Grützner's and other observers' experiments, was due to the presence of sepsis which had not been sufficiently guarded against. Raw fibrin does disintegrate in alkaline urine even in the presence of thymol, owing no doubt to the presence of bacteria in the raw fibrin, but in no instance did any digestion or disintegration take place when boiled fibrin was used. As the direct experiments with urine were negative, a large quantity was evaporated nearly to dryness at 40°, the residue thoroughly extracted, and washed with alcohol. The residue, which would contain any trypsin that might be present, was then dissolved in a small quantity of water and tested with regard to its digestive power, but the solution was found to be entirely inert. When proper precautions are taken to ensure the absence of any putrefactive change, the results are always negative.

Certain inorganic salts—potassium, sodium, and ammonium sulphates, and potassium and sodium phosphates—hinder tryptic digestion in a marked degree. This is especially the case with the potassium phosphates. J. P. L.

Physiological Action of Ethyl Lactate. By P. Pellacani and G. Bertoni (*Chem. Centr.*, 1887, 1149; from *Arch. Ital. Biol.*, 7, 201—208).—The ethyl salt of fermentation lactic acid, when taken by the mouth in concentrated solutions, causes great irritation of the throat and the first parts of the alimentary tract. When subcutaneously injected it causes no local irritation. A 10 to 15 per cent. solution does not coagulate albumin. It is a liquid, and soluble in all proportions in water, alcohol, and ether. Its hypnotic properties are weak, and its physiological action is compared with that of chloral and iodal. When given in doses sufficient to cause deep anæsthesia, it causes death by interference with the respiration. W. D. H.

Physiological Action of Trimethylethyloxyammonium and Trimethylvinylammonium Hydroxides. By V. Cervello (*Chem. Centr.*, 1887, 1150; *from Arch. Ital. Biol.*, 7, 232—233).—0·01 gram of the hydrochloride of the first base causes in the frog, dilatation of the pupil and increased frequency of respiration; after about two hours the animal returns to its normal condition. To cause complete paralysis, at least 0·05 gram must be given: death then occurs in about three hours. The pulse is but little affected. In a rabbit weighing 850 grams, 0·5 gram caused increased secretion of tears, running from the nose, and enlargement of the pupil. Paralysis, which ensues after large doses, is produced like that caused by curare. Aqueous solutions of trimethylvinylammonium hydroxide (neurine), cause the same symptoms, but its action is more powerful. The antagonism between this base and atropine holds only with regard to the heart and glandular system. Atropine will not prevent death after the administration of lethal doses of neurine. Neurine thus resembles curare in its physiological action, and muscarin in its antagonism to atropine. W. D. H.

Physiological Action of "Saccharin." By V. Aducco and U. Mosso (*Chem. Centr.*, 1887, 1148—1149; *from Arch. Ital. Biol.*, **7**, 158—171; and **8**, 22—36).—"Saccharin" (Fahlberg) is but little soluble in cold water, but dissolves more easily in hot, and very easily in boiling water. The solution so obtained is strongly acid. On cooling the hot, concentrated aqueous solution, the substance separates in monoclinic (?) needles melting at about 200°. It is more easily soluble in ether, and still more so in alcohol: it dissolves easily in water if its solution be continuously and carefully neutralised, but is reprecipitated on addition of hydrochloric acid. Even in large doses, it is harmless to the animal organism. After its administration, the urine has a well-marked, sweet taste, and decomposes with much more difficulty; it contains unaltered saccharin. It causes no alteration in nutrition or metabolism, with the exception that the chlorides of the urine are increased in amount. Saccharin is not excreted by the saliva nor by the milk. Half an hour after its administration by the mouth, the urine acquires a very sweet taste, which after doses of 5 grams disappears in 24 hours. 0·16 gram of saccharin weakens the alcoholic fermention of dextrose, as well at 30° as at 16°. A mixture of urine with an equal volume of a 0·32 per cent. solution of saccharin does not undergo the ammoniacal fermentation for over seven days, whilst urine mixed with a corresponding amount of salicylic acid ferments in less than that time. Saccharin also prevents putrefaction during pancreatic digestion. A percentage of 0·16 to 0·32 of saccharin hinders but does not prevent gastric digestion. A percentage of 0·0064 has no such effect. Benzoic acid in similar amounts has the same effect; salicylic acid a stronger effect. Saccharin hinders the amylolytic action of saliva, especially in a neutral solution, but not so much as does salicylic acid; benzoic acid, on the other hand, is not so active. As the sweetness of saccharin is 280 times greater than that of cane-sugar, it can be substituted for the latter in common use. The taste is pleasanter on neutralising and diluting. It can also be used to prevent fermentative changes in the stomach, in the urinary bladder, and for disinfection generally.

W. D. H.

Physiological Action of Santonin and its Derivatives. By F. Coppola (*Chem. Centr.*, 1887, 1206, 1208—1209, 1301—1302; *from Rend. R. Acc. Lincei* [4], **3**, 513—521, 573—578).—One per cent. solutions of santonin, of photosantonin, and of isophotosantonin in olive oil, at 38°, do not kill the ascarides lumbricoidi of the pig. Whilst, however, the two first-named substances increase the movements of the animal and cause convulsions, with isophotosantonin the reverse is the case. The other santonin-derivatives examined resemble the two first in their action on the worms. It was also found that doses of 1·25 grams of santonin daily administered to the pig did not kill the worms. The action of santonin on worms resembles its action on vertebrate animals. In order to lessen the toxic effects of the drug on the animal to which it is given it is advisable to use santoninoxime (Cannizzaro, *Rend. R. Acc. Lincei*, 1885, 703) which is insoluble in water, easily soluble in oils and fats, but not in organic acids, nor is it acted on by the gastric juice. The increased activity of the worms leads to increased peristaltic action of the intestine, which thus voids them. In the urine, santoninoxime passes out slowly as santonin; it is less poisonous than santonin, but is equally efficacious in its action on the parasites.

Experiments were also performed in order to see whether the photosantonin-derivatives differed in their action from that of santonin, and also to discover if any relation existed between physiological action and the power of solutions of these compounds to rotate the plane of polarised light. *Photosantonic acid*, $C_{15}H_{22}O_5$, has a narcotic action on frogs, doses of 0·02 to 0·03 gram abolishing first voluntary movement, then the movements of respiration; the heart and reflexes are but little affected: doses of 0·04—0·06 gram first diminish, and then abolish reflexes, and stop the heart in diastole. In vertebrate animals the action is similar, except that the reflexes are not affected. *Photosantonin*, $C_{17}H_{24}O_4$, acts in the same way, but on account of its smaller solubility the effects are not so marked. *Santonin*, $C_{15}H_{18}O_3$, itself, and sodium santonate cause as their chief symptoms convulsions; it seems then that the action of light is to modify the physiological action of these compounds on the nervous system; the action on the respiratory and circulatory systems is, however, the same. *Santonic acid*, $C_{15}H_{20}O_4$, in doses of 0·03 gram, causes no effect in frogs; 0·04 to 0·05 gram produces narcosis, abolishes respiratory movements, but does not lessen reflexes. Larger doses affect the reflexes and kill the animal; if the dose is not lethal, the animal experiences clonic convulsions like those produced by santonin, as the narcosis passes off. In a rabbit of 1 kilo. body-weight, doses of 1 to 1·5 gram applied hypodermically have no effect: 2 to 3 grams caused sleep in ½ to 1 hour, and, like santonin, epileptic convulsions. There is no action on the circulation, except with lethal doses, which stop the heart in diastole: atropine does not antagonise this action; this acid thus produces the effect of santonin combined with that of the photo-compounds, both narcosis and convulsions. Santonic and isosantonic acids act like photosantonic acid. Isophotosantonin, $C_{17}H_{24}O_4$, is no hypnotic, but easily causes strong convulsions. Isophotosantonic acid, $C_{15}H_{22[4]}O_5$, acts similarly, but is weaker. The derivatives of santonin that cause convulsions do so by their action on the medulla, not on the spinal cord. The photo-derivatives contain, like santonin, a closed naphthalene nucleus, and the differences on their constitution are to be found in the side-chains. There was found to be no connection between physiological action and the direction or amount of rotation of the plane of polarised light. W. D. H.

Physiological Action of Thallin. By G. Pisenti (*Chem. Centr.*, 1887, 1149—1150; *from Arch. Ital. Biol.*, **7**, 134—141).—Jaksch (*Zeit. Klin. Med.*, **8**) states that thallin is a strong febrifuge, but one which has no influence on the course of the disease. In the present research it was found that small doses (0·025—0·075 gram) lower the temperature of fever patients directly and considerably, but only for a short time: and as Jaksch states, there is no alteration in the course of the malady which causes the high temperature. The salt used was the sulphate. This salt hinders putrefaction, lowers the blood pressure considerably, and leaves the body by the liver and kidneys. Subcutaneous injection is not dangerous. W. D. H.

Action of Brucine and Strychnine. By T. J. Mays (*J. Physiol.*, **8**, 391—403).—It was found that in the frog the physiological effects of poisoning by strychnine and brucine respectively differ as follows:—(1.) Brucine primarily affects the posterior, whilst strychnine affects the anterior extremities. (2.) Convulsions appear very early in strychnine, and not at all or very late in brucine poisoning. (3.) Convulsions invariably develop before death occurs in strychnine poisoning, whilst death often occurs in brucine poisoning without a trace of spasm. (4.) Brucine diminishes sensibility when locally applied, whilst strychnine does not. (5.) The local anæsthetic effect of brucine appears to bear a direct relationship to its degree of freedom from strychnine. W. D. H.

Physiological Action of Caffeïne. By F. Coppola (*Chem. Centr.*, 1887, 1209—1210; *from Ann. Chim. Farm.*, **8**, 10—38).—From the result of numerous experiments on both cold- and warm-blooded animals the following conclusions are drawn:—Caffeïne does not belong to the same pharmacological group as digitalin, because it acts on the heart and the nerve-centres, whilst digitalin and the glucosides derived from it are characterised by their exclusive action on the heart. Both strengthen the heart's action by stimulation of the muscular tissue of that organ, but they act differently on the frequency of the beat. The chief difference is, however, that caffeïne causes dilatation and digitalin contraction of the blood-vessels. In many cases of cardiac degeneration where digitalis is useless caffeïne does much good.

The dilatation of the vessels produced by caffeïne renders it a valuable drug in cases of cerebral anæmia and consequent headache due to contraction of the cerebral vessels; though whether this drug would be useful in migraine it is impossible at present to say.
W. D. H.

Physiological Action of Cocaïne. By C. Sighicelli (*Chem. Centr.*, 1887, 1150; *from Arch. Ital. Biol.*, **7**, 128—133).—Cocaïne causes complete paralysis of the muscles of the eyeball, and indeed of all small striped muscles. On dropping about 1 c.c. of a 2 per cent. solution of the hydrochloride into the eye, the above takes place in about 10 minutes. It causes widening of the pupil and paralysis of the iris. It has the same action on the smooth muscles of the intestine. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Reducing and Oxidising Properties of Bacteria. By W. HERAEUS (*Bied. Centr.*, 1887, 783—784).—The author prepared pure cultivations of the various bacteria (Bacilli and Micrococci) which occur in river water, in spring water and in soil, and also of the mould fungi (*Mucor* and *Aspergillus flavus*). Besides ash constituents, the nutrient liquids contained either ammonium carbonate or calcium nitrate or carbamide. There were found (besides those bacteria that would not grow in artificial liquids) two species which reduced nitric acid to nitrous acid and ammonia, and converted carbamide into ammonium carbonate; one species which made use of nitric acid without reducing it to nitrous acid and which changed carbamide into ammonium salts; one species which behaved similarly with nitric acid, but which did not change carbamide into ammonium compounds; one species which gave no indications of action on nitrogenous substances; one species which left nitric acid unaltered but changed carbamide into ammonium salts; and lastly two mould fungi which gave no indications of action on nitrogenous substances. No species of bacteria were found which had an oxidising action; but some micro-organisms were obtained from soil infusion and from putrefying urine which converted the nitrogenous matter of both ammoniacal and urine solutions, and of diluted meat-infusion into nitrous acid.

Further an examination for oxidising properties was made with various known species of bacteria; namely, the hay bacillus, *Micrococcus prodigiosus*, Finkler's bacteria; also with the pathogenic ones, namely, those of anthrax and typhus, Tetragonus and others. In solutions containing sugar and the ash constituents, almost all of them were devoid of any perceptible growth; whilst in urine diluted with four times its bulk of water, *Micrococcus prodigiosus*, root-shaped bacteria, the spirillum of cheese, Finkler's bacteria, those of typhus and anthrax and *Staphylococcus citreus*, succeeded in forming nitrous acid. Hay bacillus, *Staphylococcus aureus*, and the bacteria of green pus and of pneumonia produced a thick turbidity but no nitrous acid. Brieger's bacteria had a feeble oxidising action, and the experiments with Miller's bacteria gave a negative result. H. H. R.

Spring Sap of the Birch and Hornbeam. By R. HORNBERGER (*Bied. Centr.*, 1887, 821—825).—The sap was drawn from the hornbeam at two spots, the one 0·7 m. the other 4·1 m. above the ground; from the birch at 0·5 m. and 3·5 m. above the ground, and the hours of collection were 10 A.M. and 6 P.M. from April 13 to May 4. The sap of both trees contains lævulose with some dextrose, nitrogen and malic acid and salts; the highest percentage of sugar is found in the sap collected at the upper boring, and the total quantity is also greater, moreover the morning sap is always richer in sugar than the evening, and if the upper opening is closed, then the sugar obtained below is in greater quantity; there appears also to be a diminution in grams per litre as the season progresses. Comparing the two saps, the hornbeam is poorer in sugar than the birch, the highest yield being 4·72 grams per litre (15·59 in the birch), and this was only obtained at the upper boring and at the commencement of the observation; ever afterwards the quantity decreased: the higher percentage of sugar in the morning sap was found in both trees. Nearly all sugar disappeared before the hornbeam ceased to blossom, whilst it still appeared up to the end of the blossoming of the birch. Malic acid is in larger quantities in both saps at the later periods, and there is no difference by day or night, but it is present in double the quantity in the birch sap, which contains least sugar. The total nitrogen in the birch sap at 3·5 m. height is twice as much as at the lower level, and the hornbeam is much poorer in nitrogen than the other tree; but little of the nitrogen appears as albuminoïds, but the albuminoïds do increase during blossoming period; the greater portion appearing as amido-acids and in other forms, even as ammonia. The mineral constituents were found to increase during the period of observation; the upper boring yielded a sap richer in minerals than the lower, and the sap is also richest when collected in the evening. With the hornbeam, this is not the case; if any difference is observable it is that the lower sap is the richest. Potash increases in the birch sap as time goes on, the evening sap being richer in it than the morning, the upper than the lower; the same holds good for lime and magnesia. Phosphoric acid increases at the lower boring as the season progresses, but it decreases at the upper; also the evening is richer in this compound than the morning sap, but it is always in larger quantities at this boring. In the hornbeam, this is different, for there is not much variation between the two yields either as time goes on or as the examination is made at evening or morning.

The bases in the birch sap are largely in excess of the mineral acid present, only ⅛ to ¼ being thus combined, and with the hornbeam there is a similar condition of affairs, only that the difference between the amounts of bases and acid is hardly so great. The author considers that the malic acid found in the sap of both trees is present as a bye-product. E. W. P.

Citric Acid in Oxycoccus Palustris. By P. Kossović (*Chem. Centr.*, 1887, 1157, *from J. Russ. Chem. Soc.*, 1887, 272—274).—The amount of citric acid found in three different samples of cranberry, *Oxycoccus palustris*, was 2·0, 2·44, and 2·8 per cent. of the total weight of the berries. As these occur very largely in many districts of the interior and the north of Russia, the author proposes to use their juice for industrial purposes, for instance in dyeing, instead of the concentrated lemon-juice imported from Italy. J. W. L.

Organic Constituents of the Beetroot Juice. By E. O. v. Lippmann (*Ber.*, **20**, 3201—3209).—Durin (*Bull. Assoc. Chem.*, **1**, No. 5) observed a thick froth, having an odour of butyric acid, to be formed on the surface of the bye-products from the preparation of sugar when being evaporated down. The author has examined the froth and found that besides the potassium salts of fatty acids, it contains dextran and phytosterin (Hesse, Abstr., 1878, 850).

Beetroot was extracted with a mixture of ether and alcohol, the ether evaporated and the residue dissolved in alcohol and treated with platinum chloride; the precipitate so obtained when purified and decomposed with hydrogen sulphide yielded lecithin. This when boiled with baryta-water yielded oleic acid, glycerol, phosphoric acid, and betaïn. The formula of lecithin is probably $C_{44}H_{82}O_9PN$.

A second experiment gave a lecithin which yielded no betaïne, but choline.

Betaïne and choline are readily separated by means of the hydrochlorides; betaïne hydrochloride forms stable crystals, whilst choline hydrochloride is very deliquescent.

Beetroot contains also other compounds containing phosphorus which are related to the nucleïns; the products of decomposition of these compounds—the xanthine compounds—are almost all contained in the molasses. (Compare Scheibler, *Annalen*, **148**, 77.)

N. H. M.

Chemico-physiological Study of Algæ. By O. Loew and T. Bokorny (*J. pr. Chem.* [2], **36**, 272—291).—Algæ (*Zygnemaceæ*) superficially dried with blotting-paper contain 85—90 per cent. H_2O; when dried at 100° their composition is—fat 6 to 9 per cent., albumin 28 to 32 per cent., cellulose and starch 60 to 66 per cent. The fat is situated chiefly in the chlorophyll region, but is not visible in drops under ordinary circumstances; lecithin is probably present. The quantity of starch varies very considerably according to circumstances; during copulation its amount decreases and glucose is formed, which otherwise very seldom accumulates in appreciable quantities. The gum is situated in the membrane, the tannin, however, in the substance of the plant. Cholesterin and succinic acid (0·4 per cent.) are also found in algæ, but the xanthines, leucine and asparagine are not present.

For *Zygnemaceæ*, nitrates are a more suitable source of nitrogen than ammonia, but this does not apply to all algæ, as some thrive very well in presence of ammoniacal salts. Potassium nitrate is far less suitable than sodium nitrate. *Spirogyræ* when placed in dilute solutions of the former died after four weeks' time, probably from overproduction of starch. Potassium chloride and potassium dihydrogen phosphate do not, however, act injuriously.

Some organic compounds (aspartic acid, succinic acid, hexamethyleneamine, &c.) act nutritiously, especially in the light, but malic and coumalinic acids cause death. Algæ live for weeks in solutions of urethane without injury; in solutions of carbamide they die after a few days, and in a few hours when placed in solutions of guanidine. On the other hand, hydantoïn and creatine act beneficially, so that the injurious action of a compound is increased when, by entrance of amido-groups, its alkalinity is increased, but lessened when, by entrance of acid radicles, its alkaline character is diminished.

Ammonia and many organic bases (ethylamine, quinoline, quinine,

&c.) cause granulation in the protoplasm of *Spirogyræ*, and death results, probably owing to polymerisation of the active albumin; their hydrochlorides act similarly, but in a less degree; it is probable, however, that ammonia salts do not act banefully when added in such quantity that the production of albumin and consumption of ammonia keep pace with the supply of the latter. Many other substances (nitrous acid, hydrocyanic acid, potassium chlorate, &c.) cause death more or less quickly, but numerous salts (sodium phosphite, hypophosphite, thiosulphate, barium chloride, potassium ferrocyanide, &c.) have no harmful action.

Algæ kept in the dark lose their starch more rapidly when the temperature is increased; a supply of peptones, however, decreases the rapidity of the absorption. Starch is not produced by *Spirogyræ* when the algæ are placed in a solution containing 0·1 per cent. of sugar; *Vaucheria*, though it produces no starch when placed in a 5 per cent. sugar solution, forms a little when placed in a 20 per cent. solution. *Spirogyræ* deprived of its starch lived in the dark for three weeks in a 0·1 per cent. solution of methylal, but no starch was formed. At the end of this time it was exposed to the light in water containing carbonic anhydride, whereupon starch was produced; a second portion of the same plant died in about three days under similar conditions, but without the addition of methylal. *Vaucheria* placed in 0·2 per cent. methylal solution sent off numerous shoots, whilst in water alone the growth was quite inconsiderable; a 1 per cent. methylal solution can be borne by *Vaucheria* for several days, but in a 0·05 per cent. solution of formaldehyde death soon ensues.

It follows, therefore, that methylal serves as nourishment for algæ, although starch is not formed from it, but it seems that a carbohydrate is first formed which is suitable for the production of cellulose, and the authors conclude that Baeyer's theory of the formation of starch is the correct one, not only from the result of their own experiments, but because it is supported by other facts, especially by the rapid growth of bacteria in solutions containing compounds of methyl. F. S. K.

Effects of Atmospheric Deposits on Plants and Soil. By E. Wollny (*Bied. Centr.*, 1887, 721—723).—The author has experimented on this subject, employing flower pots with closed bottoms and of about 4 litres capacity. These were filled with a soil rich in humus, containing in different pots amounts of water varying from 10 to 100 per cent. of the quantity the soil could hold when fully saturated. The plants experimented on were peas, rye, rape, and a grass mixture. Additions of water were made from time to time to make up for evaporation and preserve a constant degree of moistness. At the end of the experiments the crops were weighed. The following results were obtained:—1. A proper supply of water is by far the most potent factor in producing a good crop. 2. Up to a certain limit, increase of water gives increased yields, but beyond that limit further increase of water produces a continuous diminution in yield, which falls almost to zero when complete saturation of the soil is reached. 3. Within the limit mentioned, different plants are affected in different degrees by the amount of water. 4. The most favourable amount of water is different at different stages of growth.

The observations that have been made up to date lead to the conclusion that the maximum yield is obtained within a limit lying between 40 and 80 per cent. of the amount of water the soil can hold when fully saturated. In the case of each particular plant, the amount of water giving the best yield is higher, the more fertile the soil, the more the climate favours the development of the organs of transpiration, and the closer together the plants are situated. As regards the duration of growth, the smaller the water supply the shorter this period is, and in a drought the plants are more liable to die before they are perfectly developed, and to become prematurely ripe the closer they are together. The chemical composition of the grain is also affected by the supply of water; analysis shows that dryness of soil favours the development of a compact, glassy grain rich in nitrogen, whilst in moist situations the grain is less compact in texture, more mealy, and proportionally poor in nitrogen.

H. H. R.

Testing Soil by the Growth of Oats. By A. ATTERBERG (*Bied. Centr.*, 1887, 723—728).—At the Calmar experimental station in Sweden, a soil suspected of having a deficiency of nitrogen and magnesia was examined as follows:—Portions of it placed in tin vessels were sown with black bearded oats, which were manured in some cases with nitrogen, in others with magnesia, and in others no manure was applied. Part of the plants were cut when the panicle had emerged from the sheath, and the rest when the oats were fully ripe. The results were determined as regards (1) the oats cut green, (2) the ripe straw, and (3) the ripe grain.

Where magnesia had been applied, the results were negative. From the comparison of the oats manured with nitrogenous manures with the unmanured crop the following inferences are drawn:—(1.) Liberal nitrogenous manuring considerably increased, not only the weight of the crop, but also the amount of nitrogen both in the ripe and unripe plant. (2.) This was accompanied by a material diminution in the amounts of potash and silica. (3.) The amounts of lime and magnesia were less affected. (2) and (3) are attributed to the fact that the soil, which was very poor in nitrogen, was not rich enough in available potash and phosphates to properly meet the demands of the luxurious vegetation induced by the nitrogenous manuring, but was rich enough, however, in lime and magnesia.

This suggested experiments with potash and phosphates in addition to nitrogen as manuring agents, and these experiments showed—1. That manuring with phosphates produced an increase of phosphoric acid throughout the plant, whilst, notwithstanding that the crop had not increased, the amount of nitrogen diminished in the cases of the plants cut green and of the ripe straw. 2. That manuring with potash was accompanied by a material increase of crop, and that here not only was the amount of potash raised, but also the amounts of nitrogen and phosphoric acid were considerably lowered in both the plants cut green, the ripe straw, and the ripe grain.

The author also conducted some sand culture experiments on the same kind of oats by Hellriegel's method, and found equally remarkable relations among the constituents.

In the first set, varying quantities of nitrogenous manures were applied, and the results showed that the smaller the application of nitrogen, the smaller is the amount of it in the plant and the greater is the amount of phosphoric acid, of magnesia, and in most cases of potash and lime.

In the second set, varying quantities of phosphates were applied, and the results showed that the smaller the application of phosphates the smaller is the amount in the plant, and the greater is the amount of nitrogen and of potash. In the grain, the amounts of potash and magnesia are more constant, and the amount of magnesia appears to follow that of the phosphoric acid.

In the third set, varying quantities of potash were applied, and the results showed that the smaller the application of potash, the smaller is the amount of it in the plant, whilst the amounts of nitrogen, phosphoric acid, and magnesia rise regularly. This did not hold in cases where the growth of the plant was checked, for here the composition was that of the unripe plant.

In the fourth set, varying quantities of magnesia were applied, and the results showed that the smaller the application of magnesia, the greater is the amount of nitrogen and phosphoric acid, at least in the unripe plant and in the straw; the amount of lime also increases regularly.

The author sums up thus:—In the case of a plant-food, if the quantity available for the plant diminishes, then diminishing amounts of it are taken up and assimilated, and the quantity in the plant also sinks. This is accompanied by a feebler development of the plant, and consequently by a smaller crop; thus the other foods are in excess relatively to the food present in a minimum degree, and so are taken up and assimilated in increasing quantities. H. H. R.

Influence of Lime as a Soil Constituent on the Development of Plants. By E. W. Hilgard (*Bied. Centr.*, 1887, 738—739).—In general, the effect of a large proportion of lime is to encourage a low, compact growth and increased fruitfulness, whilst a deficiency of lime in a soil, otherwise of good composition, produces a thin growth and diminished fruitfulness. The droughty territories of Arizona, California, and Oregon show this on a large scale in the low and compact forms of their trees, which are less due to the parching sun than to the high proportion of lime, all the greater there for the want of a liberal rainfall to dissolve it away. H. H. R.

Injury to Vegetation by Sulphurous Acid. By L. Just (*Bied. Centr.*, 1887, 790).—The injury which some mangolds planted near a cellulose factory had suffered, proved on chemical investigation to have been due to the sulphurous acid in the gases from the factory.

The figures obtained show that the amount of sulphuric anhydride in the diseased plants is abnormal, and is higher than in the uninjured ones. H. H. R.

Manuring Hops. By C. KRAUS (*Bied. Centr.*, 1887, 785—786).—In general the manure should contain three plant-foods, phosphoric acid, potash, and nitrogen, and contain some organic substance, which by its decay will slowly render those foods available. Guano made from fæces in moderate dressings is preferable to the potash-ammonia-superphosphate formerly recommended; it acts better even than mixtures of sodium nitrate and superphosphate containing the same amounts of plant-food. Rape-cake meal would appear to be suitable on the above grounds, and in France it has been found to give good results. These manures are like farmyard manure both in chemical nature and physical effects, and, as with farmyard manure, care must be taken to avoid over manuring. Although nitrogen is of the greatest importance to the hop, as it is to other plants, yet it is possible to give too much of it, and so cause injury. If nitrogenous manures are employed alone on the poorer soils, the yield will not be a full one, and even on the better soils the crops will in time fall off. Potash and phosphates should only be employed without nitrogen when a trial has proved that there is enough nitrogen stored up in the soil, and that nitrogenous manuring will not increase the yield without injuring the quality.

In good situations, artificial manure in addition to farmyard manure is the best means of realising the profit which the locality affords.

H. H. R.

Manuring Sugar Beets with Basic Slag. By E. v. PROSKOWITZ (*Bied. Centr.*, 1887, 739—742).—The trial was made in Kwassitz on an alluvial soil in low marshy country. The plots were 100 square metres (0·025 acre) in area. The manures employed were a basic slag and a superphosphate. The slag contained 20·5 per cent. of phosphoric anhydride, only 0·04 per cent. being soluble in citrate solution. Its state of division was one of medium fineness. The superphosphate contained a total of 17·3 per cent. of phosphoric anhydride, 12·44 per cent. being soluble in water.

The unmanured plots all suffered from root decay. The best matured roots (as indicated by their having the smallest proportion of leaves to roots) were on the plots manured with superphosphate. The author concludes that in that particular neighbourhood, on heavy clay land, the basic slag was less effectual than the customary quantity of superphosphate, and that the time of applying it had no decided influence.

H. H. R.

Comparison of the Different Properties and Character of Manure made with Straw and with Turf Litter. By M. FLEISCHER (*Bied. Centr.*, 1887, 808—814).—As regards the value of straw or peat alone as manure, it appears that straw contains most potash, lime, and phosphoric acid, whilst peat moss litter contains most nitrogen, and when mixed with manure the peat manure contains more easily soluble nitrogen than the straw manure; the retention of soluble nitrogen (ammoniacal compounds) by peat therefore renders it somewhat more valuable than straw. Field experiments show that peat makes the better manure, especially on light land, because of its retentive capacity for soluble nitrogen, consequently the after effects are greater than when straw is employed. On heavy lands, however, the question is not yet decided. E. W. P.

Behaviour of Various Plants towards Nitrogenous Manures. By E. Wolff and C. Kreuzhage (*Bied. Centr.*, 1887, 793—808).—The object in view was not to estimate the capability of plants to absorb nitrogen from the air either directly or indirectly, but rather to collect facts to prove that various plants are differently influenced by nitrogenous manures. To this end plants were sown in artificial soils, the base being sand, in some cases calcined, in others in the ordinary state, and the experiments extended over some years. Some plants received no added nitrogen, whilst others received increasing quantities. Full details of the weight of the crops harvested, the manures, &c., are given. The yield of straw crops (oats, &c.) is greatly increased by the addition of Chili saltpetre, but Leguminosæ, beans, lupines, clover, &c., are not increased in yield even when the amount of added nitrogen is trebled. Beans, &c., remove from the soil more nitrogen than is contained in the original seed and the manure, whilst the opposite is the case with oats, &c. E. W. P.

Analytical Chemistry.

Gas Receiver for Absorption Analyses. By F. A. Wilber (*Amer. Chem. J.*, **9**, 418—420).—A peculiar form of eudiometer intended for the analysis of the gases obtained from potable waters.

Use of Asbestos for Assisting the Subsidence of Suspended Matter. By W. Fresenius (*Zeit. anal. Chem.*, **27**, 32—33).—In cases where, owing to the presence of very finely divided suspended matter, as in experiments on artificial digestion, it is difficult to get clear filtration, the subsidence of the solid particles may be greatly assisted by vigorously shaking with fibrous asbestos. M. J. S.

Determination of Sulphur, Chlorine, Bromine and Iodine in Organic Compounds. By P. Clason (*Ber.*, **20**, 3065—3066).—This method consists in burning the substances in air charged with nitric acid. The nitric acid is contained in rolls of platinum gauze 5 cm. long and 1 cm. in diameter, filled with very small glass beads; these rolls absorb the acid readily, and it does not run out when the rolls are placed horizontally. The combustion tube is connected at one end to the air supply, then come two nitric acid rolls, a roll without nitric acid, boat containing the substance, two rolls without nitric acid placed a small distance apart, after an interval two more nitric acid rolls, and lastly a roll without acid; the end of the tube is drawn out, bent downwards, and dips into a flask containing water, or, in the case of chlorine and bromine combustions, a solution of silver nitrate. The combustion is conducted in the usual manner, the empty rolls in the front part of the tube being first heated to redness, and the substance and acid rolls then so heated that a steady stream of nitrous fumes issues from the exit tube. A. J. G.

Comparative Value of some Proposed Tests for Nitric Acid. By P. Walden (*Chem. Centr.*, 1887, 1180—1181, from *J. Russ. Chem. Soc.*, 1887, 274—295).—Brucine gives a feeble coloration with solutions of potassium nitrate, 1 : 500000, and of potassium nitrite, 1 : 1100000. Diphenylamine is equally delicate. The author does not recommend phenol or toluidine. For nitrous acid, diamidobenzoic acid, metaphenylenediamine, naphthylamine and amidobenzeneorthosulphonic acid are recommended, their delicacy being 1 : 5000000. The colour reaction with naphthol is not characteristic for nitric and nitrous acids nor for chlorine; it is much less delicate than the brucine and diphenylamine tests. Nitric and nitrous acids in presence of other oxidising agents can be detected in the following way :—Concentrated sulphuric acid and the solution in question are added to an alcoholic solution of β-naphthol. The solution is coloured red, yellowish, or cinnamon, and shows fluorescence, which is not caused by the other oxidising agents. The delicacy is one in 300,000. These reagents can only be used as group reagents, the colours being produced by any energetic oxidising agent. If nitric and nitrous acids are both present, the former can be detected by the compounds mentioned with toluidine. The nitrous acid is then destroyed by an excess of carbamide and sulphuric acid, and the nitric acid which has remained unchanged can be detected by means of brucine or diphenylamine. In water analysis, where there are no other oxidising agents present, brucine, diphenylamine, and metaphenylenediamine are to be preferred to zinc iodide and starch-paste. The author finally recommends a solution of diphenylamine in concentrated sulphuric acid as a reagent for chromic acid, which produces quickly a fugitive blue colour even with a dilution of one part potassium dichromate in 700,000. J. W. L.

Presence of Sodium Phosphate in Glacial Phosphoric Acid. By A. Bettendorff (*Zeit. anal. Chem.*, **27**, 24—26).—The phosphoric acid in sticks found in commerce frequently contains sodium phosphate, which communicates hardness to the otherwise soft glassy acid. It can be detected by dissolving the solid in fuming hydrochloric acid, when the sodium remains undissolved as chloride. A quantity of sodium pyrophosphate (ignited to destroy organic matter) dissolved in hydrochloric acid of 1·19 sp. gr., left 98·5 per cent. of its sodium as chloride. One part of sodium chloride requires 1348 parts of this acid at 12° for its solution. This furnishes a direct method of preparing phosphoric acid from sodium phosphate. M. J. S.

Estimation of Phosphoric Acid in Basic Slag. By G. Kennepohl (*Chem. Zeit.*, **11**, 1089—1091).—The author confirms the opinion expressed by Klein (Abstr., 1886, 835), that there is little or no iron phosphide in basic slag. The phosphoric acid in basic slag may be accurately determined in the following manner: 10 grams of the finely powdered slag (moistened with alcohol to prevent adherence) placed in a 500 c.c. flask, is heated with 40 c.c. of hydrochloric acid, sp. gr. 1·12, and 40 c.c. of water, for at least a half an hour on a water-bath; if much ferrous salt is present, it is well to add a little nitric acid or bromine before heating. An aliquot part of the filtered solution is mixed with ammonium nitrate and molybdate solution, without previous removal of the silica. The solution, after heating at about 80° for 15 minutes, is filtered, and the precipitate washed with water containing 3 per cent. of nitric acid (to remove adhering iron salts), redissolved in 2·5 per cent. ammonia, and then precipitated with magnesia mixture. The presence of silica does not interfere, owing to the ready solubility of ammonium silicomolybdate in the washing water. D. A. L.

Estimation of Arsenic in Pyrites. By H. Fresenius (*Zeit. anal. Chem.*, **27**, 34—35).—To ascertain whether by fusion the whole of the arsenic could be obtained in alkaline solution, about 10 grams of pyrites was intimately mixed with two parts of sodium carbonate and one part of potassium nitrate. The mixture was fused and thoroughly exhausted by boiling with sodium carbonate solution. The filtrate was neutralised with hydrochloric acid, mixed with ferric chloride, and precipitated by calcium carbonate. The precipitate was distilled with ferrous chloride and hydrochloric acid as long as arsenic passed over. The undissolved residue from the fusion was also dissolved in hydrochloric acid and distilled with ferrous chloride. In the latter distillate, about 9 per cent. of the whole quantity of arsenic was found. The method therefore presents no advantages over direct distillation in a current of chlorine, or distillation with ferrous chloride, after dissolving in hydrochloric acid with addition of potassium chlorate. M. J. S.

Estimation of Oxygen, Carbonic Anhydride and Carbonic Oxide. By J. Sinibaldi (*Bull. Soc. Chim.*, **48**, 244—246).—An apparatus somewhat resembling Elliott's gas analysis apparatus in principle, but not intelligible without the diagram. C. H. B.

Apparatus for Direct Determination of Carbonic Anhydride. By O. Ostersetzer (*Zeit. anal. Chem.*, **27**, 27—30).—A conical flask of 70 c.c. capacity is closed with a caoutchouc stopper bored with two holes. Through one passes a tube bent at a right angle. This is the inlet for washed air. Below the stopper the diameter of this tube is reduced so that when raised it is loose in the hole. Near its lower end it has a glass hook on which is hung the glass bucket containing the carbonate. At the end it is drawn out to a point which is turned upwards. The other hole carries a Welter's safety bulb tube joined to a Geissler's drying tube. Both of these contain sulphuric acid. Into the upper end of the Geissler's tube is ground a small cylinder for holding pumice saturated with copper sulphate, and the potash bulbs for absorbing the carbonic anhydride are directly connected to the upper end of this. To use the apparatus, the inlet tube is raised, and the bucket containing the substance is hung on its hook. A small excess of highly dilute acid is placed in the flask, and all the connections are made. The tube carrying the bucket is then pushed down into the acid, its wider portion immediately making it fit tight in the stopper. Purified air is gently aspirated through during the decomposition, and finally the flask is shaken and gently warmed.

M. J. S.

Analysis of German Silver. By F. Oettel (*Zeit. anal. Chem.*, **27**, 15—18).—This alloy consists of copper, nickel, and zinc, but may also contain tin, lead, iron, cobalt, and manganese. The copper can with certainty be separated from zinc by one precipitation by hydrogen sulphide from a sulphuric acid solution, although not from a nitric acid solution. The solution of 0·5 gram of the alloy in nitric acid (which is consequently free from tin), is evaporated with sulphuric acid, which removes lead. It is then diluted to 100 c.c., acidified with 2 c.c. of strong hydrochloric acid, and precipitated by hydrogen sulphide. It is heated to boiling and re-cooled before filtering, and the precipitate is washed with dilute aqueous hydrogen sulphide, adding a little hydrochloric acid at first.

The filtrate is evaporated to remove hydrochloric acid, diluted, neutralised with potash, mixed with a few drops of sodium acetate, and saturated in the cold with hydrogen sulphide; zinc sulphide separates in a pulverulent form, easily filtered and washed. The hydrogen sulphide is removed from the filtrate by boiling, the iron is oxidised by bromine (not by nitric acid), and precipitated by ammonia. The concentrated filtrate is made strongly alkaline with ammonia and electrolysed. Nickel and cobalt are deposited together on the platinum cylinder, whilst the manganese separates as hydrated peroxide. Precipitation of the nickel by an alkali is only to be trusted when performed in platinum vessels. The copper and lead can also be determined electrolytically. By electrolysing a nitric acid solution of the nitrates with four small Daniell cells, the copper from 0·5 gram of the alloy can be completely deposited in three hours, the lead at the same time separating as peroxide which can be weighed. If a sulphuric acid solution is electrolysed, the copper separates as a red mud, which can be filtered off after stopping the current, leaving the other metals for determination as above. M. J. S.

Separation of Aluminium and Beryllium. By A. Zimmermann (*Zeit. anal. Chem.*, **27**, 61—63).—Of all the processes hitherto proposed that based on the precipitation of beryllia, when its solution in potash is boiled, seems to be the best. A very pure potash (purified by alcohol and heated till free from organic matter) is requisite. The solution of 0·3 gram of substance must not exceed 300 c.c., or alumina will be precipitated with the beryllia. After 15 to 20 minutes' boiling in a platinum basin much hot water is added, and the beryllia is filtered off and washed. It is free from potassium.

When the two earths are present in about equal quantities, but not otherwise, they may be completely separated by neutralising with sodium carbonate and boiling with thiosulphate until no more sulphurous acid is given off; 15 to 20 hours' boiling is sometimes necessary. The alumina is precipitated together with sulphur.

M. J. S.

Determination of Alumina in Presence of Iron and Phosphoric Acid. By L. Blum (*Zeit. anal. Chem.*, **27**, 19—24).—In the technical analysis of such a mixture, it is usual to determine iron and phosphoric acid in two portions of the solution, to precipitate a third by ammonia, and estimate the alumina from the difference. The iron is best determined by precipitation as sulphide after adding tartaric acid. Permanganate gives higher results, owing probably to the presence of organic matter.

The author draws attention to the risk of error in the precipitation of alumina by ammonia. An excess of ammonia re-dissolves the precipitate. The common practice is therefore to boil until the odour of ammonia becomes exceedingly faint. When, however, ammonium chloride is present, the detection of ammonia in the steam by the sense of smell is compatible with an acid condition of the liquid caused by dissociation of the ammonium chloride, and in such a case part of the alumina will be re-dissolved. Presence of ammonium chloride, however, diminishes the solubility of alumina in ammonia, and by using only a small excess of ammonia, and boiling for only a short time, then filtering and washing rapidly, and only with hot water, no loss will be incurred. M. J. S.

Determination of Traces of Bismuth and Antimony in Commercial Copper. By P. Jungfer (*Zeit. anal. Chem.*, **27**, 63—65). —On adding sodium carbonate to a nitric acid solution of copper containing bismuth, the latter is precipitated first. After vigorous stirring and remaining for an hour or two, the precipitate can be filtered off, dissolved in a little hydrochloric acid, and the bismuth precipitated as oxychloride by diluting. If on dissolving the copper in nitric acid a residue remains, this should be fused with sodium carbonate and sulphur, and tested for bismuth by Hampe's method (*ibid.*, **13**, 184). The separation of arsenic and antimony from copper by conversion into iodides (Flajolot), is only satisfactory in the case of arsenic, but the addition of potassium fluoride greatly facilitates the washing out of the antimony from the cuprous iodide, owing seemingly to the formation of the highly soluble potassium antimonious fluoride. To the solution of 10 grams of copper in 50 c.c. of nitric acid of 1·4 sp. gr., after dilution to 200 or 300 c.c. with cold water, 0·15 gram of potassium fluoride is added, and then 26·2 grams of potassium iodide in small portions alternately with sulphurous acid. Excess of iodide is to be avoided. The liquid is then heated until the precipitate has completely subsided. The precipitate is washed with hot water containing sulphuric acid. After removing the excess of sulphurous acid from the filtrate by iodine, hydrogen sulphide is passed in. The precipitate is dissolved in hydrochloric acid with addition of potassium chlorate, and after adding tartaric acid and ammonia, the copper, lead, and bismuth are thrown down by the cautious addition of dilute hydrogen sulphide, leaving the arsenic and antimony in the filtrate to be separated by the usual methods. M. J. S.

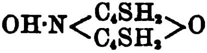
Estimation of Dissolved Carbonic Anhydride in Water. By L. VIGNON (*Compt. rend.*, **105**, 1122—1124).—50 c.c. of recently distilled water or of a well-boiled sample of the water to be tested is mixed with 10 drops of a saturated alcoholic solution of phenolphthaleïn and a standard solution of lime water is added until a pink colour is developed.

50 c.c. of the water to be tested is treated in precisely the same way, the standard solution being added until the intensity of the coloration is the same in both tubes. Towards the end of the titration, a little time must elapse between successive additions of the calcium hydroxide. The difference between the volume of alkali required in the two cases gives the amount of free carbonic anhydride.

Chlorides, sulphates, and nitrates of calcium or magnesium do not affect the result, but if the water contains magnesium carbonate, or alkaline salts the acids of which form insoluble compounds with calcium, a sufficient quantity of neutral calcium chloride should be added to convert the magnesium and the alkalis into chlorides. If the second liquid becomes so turbid that comparison of the tints is difficult, some calcium carbonate may be added to the liquid in the first tube.

This method will estimate 1 c.c. of carbonic anhydride dissolved in 1000 c.c. of water. C. H. B.

Estimation of Ash in Organic Substances. By A. KÖBRICH (*Chem. Zeit.*, **11**, 1159).—5 or 10 grams of the substance is submitted to a preliminary burning in a platinum dish, the latter being preferred to a crucible, as the chance of loss by creeping over the side is less. If the substance burns readily, the ignition is completed in the dish; if otherwise, the char is pulverised, transferred to a platinum crucible, and the ignition completed in a current of oxygen; the operation proceeds quietly without any spluttering, as is the case when ammonium nitrate is used. When particles of carbon are enclosed by the fusion of the ash, it is recommended to dissolve the mass in water; the particles of carbon rise to the surface, and after careful evaporation are easily oxidised by igniting. D. A. L.

Thiophen Reaction with Nitrous Sulphuric Acid. By C. LIEBERMANN (*Ber.*, **20**, 3231—3234).—This reaction was mentioned in 1883 (*Ber.*, **16**, 1473), but seems to have been overlooked, as one practically identical with it, has just been given by Claisen and Manasse (*Ber.*, **20**, 2197). Two or three drops of sulphuric acid containing nitrous acid are shaken for some time with 1 c.c. of the benzene under examination, when the acid gradually acquires a corn flower-blue colour. If much thiophen is present, the reaction occurs almost at once; with 2 to 3 per cent. of thiophen, it appears after a few minutes, whilst with very small quantities some 10 to 15 minutes is required for its complete development. As little as 0·25 milligram of thiophen can be detected by this test. The colouring matter is precipitated on dilution with water as a deep-brown, flocculent substance, soluble in sulphuric acid, with deep-blue colour, insoluble in water. It seems to have the constitution  $OH{\cdot}N{<}\genfrac{}{}{0pt}{}{C_4SH_2}{C_4SH_2}{>}O$; atmospheric oxygen is absorbed in its formation; hence the necessity of the continued shaking. A. J. G.

Examination of Cane-sugar for Sulphurous Acid. By DAVIDSEN (*Chem. Centr.*, 1887, 1180, from *Deut. Zuckerind*, **12**, 939).—The sugar is dissolved in a few c.c. of cold very dilute starch solution. To this a few drops of iodic acid are cautiously added, so that the liquids do not mix. A blue ring appearing at the junction shows the presence of sulphurous acid (or thiosulphuric acid). This method can also be used as a quantitative one by titration with iodine.

J. W. L.

Detection and Direct Estimation of Starch in Liquids containing Dextrin. By G. BURKHARD (*Chem. Zeit.*, **11**, 1158).—The liquid containing starch and dextrin is well mixed with just sufficient alcohol to produce a slight turbidity; it is then warmed until the turbidity disappears. Tannin solution is now added to this weak alcoholic solution, and when cold the starch precipitate is collected. For qualitative purposes, the precipitate can be simply tested on the filter with dilute iodine solution. For quantitative work, the tannin is washed from the precipitate by means of alcohol; the filter and precipitate are then transferred to a Lintner's pressure flask, and mixed with 20 c.c. of water and 1 c.c. of normal sulphuric acid. After heating for four hours at below 115°, the contents of the flask are neutralised with 1 c.c. of normal soda, filtered, and the sugar determined by Fehling's solution, using Allihn's tables for converting the quantity of reduced copper formed into sugar, and multiplying this figure by 0·9 to find the amount of starch present. D. A. L.

Detection and Estimation of Aldehydes in Commercial Alcohols. By U. GAYON (*Compt. rend.*, **105**, 1182—1183).—The author utilises the well-known fact that aldehydes and ketones produce a red coloration in solutions of magenta which have been decolorised by sulphurous acid.

In order to prepare the reagent, a solution of 1 gram of magenta in 1000 c.c. of water is mixed with 20 c.c. of a solution of sodium hydrogen sulphite of 30° B. After about an hour, when the liquid has become nearly colourless, 10 c.c. of pure concentrated hydrochloric acid is added. The order of mixing is important. The reagent is preserved in small, well-closed bottles, and becomes more sensitive on keeping.

The alcohol to be examined is mixed with water until its strength is approximately 50°, and 2 c.c. of the diluted liquid is mixed with 1 c.c. of the reagent. A rose-violet colour appears in a few minutes, the reaction being sufficiently delicate to detect one part of aldehyde in 500,000 parts of alcohol.

Quantitative estimations are made by comparing the depth of tint produced by the alcohol under examination with that produced by alcohol containing a known proportion of ordinary aldehyde, the results being expressed in terms of the latter. C. H. B.

Analysis of Materials containing Tartaric Acid. By N. v. Lorenz (*Zeit. anal. Chem.*, **27**, 8—14).—Goldenberg's method (*ibid.*, **22**, 270), as modified by the author, is carried out as follows:—15 grams of the finely ground substance (argol or lees) is boiled with 250 c.c. of water and 6 grams of potassium carbonate for 20 minutes with stirring, in a basin of at least 700 c.c. capacity over a free flame. After cooling, it is made up to 500 c.c. If the substance is calcium tartrate only 7·5 grams is taken, and is made up to 250 c.c. It is filtered, and 100 c.c. of the filtrate is evaporated on the water-bath as far as is possible without any salt depositing. While still hot, it is mixed with 5 c.c. of glacial acetic acid, and as soon as effervescence has ceased 100 c.c. of absolute or 95 per cent. alcohol is added. It is vigorously stirred for two minutes, allowed to remain for 15 minutes, but not longer, then the potassium hydrogen tartrate is collected by suction through a filter of 50 c.c. capacity, on which it is washed once with 50 c.c., and twice with 25 c.c. of absolute alcohol. Without drying, it is thrown with its filter into the precipitating basin, boiled with 200 c.c. of water, and titrated hot with 3/10 normal soda, boiling for five minutes, when the end is approached. A neutral decoction of litmus is used, the preparation of which is minutely described. The original solution obtained by boiling the substance with potassium carbonate must be alkaline. If, owing to the presence of much calcium sulphate, this is not the case, a fresh portion must be boiled with 12 grams of carbonate. Direct experiments show that considerable variations in the quantity of potassium carbonate used do not affect the result. On the other hand, the quantity of acetic acid prescribed must be adhered to. The 200 c.c. of alcoholic filtrate retains in solution about 0·0177 gram of potassium hydrogen tartrate, corresponding with 0·59 per cent., but this loss is to a great extent compensated for by neglecting the volume of the insoluble matter, although in the case of lees an additional 5 c.c. of water should be added in making up to partially allow for this. M. J. S.

Points of Difference between Linseed Oil and Linseed-oil Varnish. By Finkener (*Chem. Zeit.*, **11**, 905—906).—In columns 15 mm. thick, the oil appears yellow, the varnish brown, by transmitted light. When smeared on a plate, the oil remains greasy for 24 hours, whilst the varnish becomes sticky, or even solidifies. The following test will distinguish a pure linseed oil from an oil containing 25 per cent. of the varnish. 12 c.c. of the oil under examination is shaken with 1 c.c. of a 20 per cent. solution of ammonia mixed with 5 c.c. of the test solution (composed of 100 grams of lead acetate, 150 c.c. of water, and 32 grams of glycerol), and heated at 100° for three minutes; linseed oil forms two liquid layers, the lower one clear as water; whereas linseed-oil varnish sets to a salve-like mass. So-called bleached linseed-oil varnish is paler yellow than linseed oil, nevertheless it resembles the latter in other points. With solvents, saponifying and oxidising agents, the behaviour of the oil is not readily distinguishable from that of the varnish. D. A. L.

Apparatus for the Estimation of Urea. By P. CAZENEUVE and HUGOUNENQ (*Bull. Soc. Chim.*, **48**, 82—86).—This apparatus consists of a copper oil-bath, provided with a thermometer and thermoregulator, and bronze tubes fitted with screw-caps, coated internally with platinum by electrolysis, and capable of withstanding a pressure of 60 atmos.

25 to 30 c.c. of the liquid to be examined is agitated with unwashed bone-black, which decolorises and neutralises it, and 10 c.c. of the filtered liquid is diluted with 20 c.c. of water, heated in one of the tubes at 180° for half an hour, and the ammonia formed is estimated by titration with normal sulphuric acid, using methyl-orange or phenolphthaleïn as indicator. The results of the test analyses given are very satisfactory. Hugounenq has previously shown that tyrosine, leucine, peptones, &c., give no ammonia when heated with water at 180—190°. C. H. B.

Note by Abstractor.—Phenolphthaleïn is useless as an indicator in presence of ammonium salts or for the titration of ammonia.—C. H. B.

Volatile Alkaloïds. By O. DE CONINCK (*Compt. rend.*, **105**, 1180—1182).—A summary of the methods available for distinguishing the volatile alkaloïds from one another. Details of the application of these methods will be given in a subsequent paper. C. H. B.

General and Physical Chemistry.

Degree of Oxidation of Chromium and Manganese in Fluorescent Compounds. By L. DE BOISBAUDRAN (*Compt. rend.*, **105**, 1228—1233).—This paper contains details of the results obtained by calcining, in air or in hydrogen, mixtures of pure alumina with chromic oxide; of gallium oxide and chromic oxide; of calcium oxide and chromic oxide; of magnesium oxide and chromic oxide; of alumina with small quantities of potassium and manganese oxides; and of calcium and manganese oxides.

Too large a proportion of chromium reduces and may even destroy the fluorescence. In some cases, calcination in hydrogen reduces, in others it intensifies the fluorescence, but no general conclusions are drawn as to the influence of the degree of oxidation on the phenomenon. C. H. B.

Rotatory Dispersion. By L. GRIMBERT (*J. Pharm.* [5], **16**, 295—300; 345—350).—The author employed Laurent's polarimeter and monochromatic light. To obtain rays near to C, a layer 1 cm. thick of the following solution was used:—Carmine No. 40 0·25 gram, ammonia 20 c.c., water to make up to 100 c.c. With white light, this solution gives a spectrum reduced to a very narrow band coinciding with the C line. On taking the rotative power of an active substance in this light and also in the sodium light, two different values are obtained, $[\alpha]_D$ and $[\alpha]_C$. The ratio $[\alpha]_D/[\alpha]_C$ gives the dispersive power. Usually tubes of 200 mm. length were employed; sometimes 100 mm. tubes were used, as, for example, when the deviation was over 20°.

Saccharose.—Both water and alcohol were employed as solvents. The rotative power varies neither with the concentration nor with the solvent: $[\alpha]_D = +66·45°$; $[\alpha]_C = 52·85°$; and $[\alpha]_D/[\alpha]_C = 1·257$.

Lactose.—It is well known that the rotative power of lactose diminishes rapidly when first dissolved in the cold. The rotative power does not vary with the concentration. It is $[\alpha]_D = +52·37$ and $[\alpha]_C = +41·58°$. The ratio between the rotative power when first dissolved to that when it becomes stationary is as 8 : 5. The dispersive power is $[\alpha]_D/[\alpha]_C = 1·259$, and is constant during the time the rotative power is passing to the minimum. It does not vary with the concentration of the solution.

Maltose.—When dissolved in the cold, the rotative power of maltose increases to a maximum. Its dispersive power is 1·262, and is constant during the time the rotative power is changing.

Glucose acts like lactose. The ratio between the initial and final rotative powers is as 2 : 1. The dispersive power is 1·258, and is constant whilst the rotative power is passing to the minimum.

Morphine Hydrochloride.—Solutions of different degrees of concentration confirmed the value given by Hesse, $[\alpha]_D = -100·67° - 1·14\,C$.

The dispersive power $[\alpha]_D/[\alpha]_C = 1{\cdot}284$, and does not vary with the concentration.

Codeïne.—In absolute alcohol, $[\alpha]_D = -134{\cdot}24°$, and in chloroform $-114{\cdot}82°$, but the dispersive power only varies slightly and is on the average 1·268.

Brucine.—Anhydrous brucine, dissolved in absolute alcohol and in chloroform, gave values for $[\alpha]_D$ confirming those obtained by Oudemans. The dispersive power does not vary with the nature of the solvent, and is = 1·357, the highest hitherto observed.

Quinine.—The hydrate, dissolved in absolute alcohol, and in chloroform; the basic hydrochloride dissolved in water; and the normal sulphate dissolved in water, and in 90° alcohol, all give the same dispersive power of 1·313, the variation in the solvent and in the acid combined with the base producing no change in this respect.

Cinchonine.—The basic sulphate was observed when dissolved in water, absolute alcohol, and chloroform. Although the nature of the solvent has considerable effect on the rotative power of the salt, the dispersive power remains constant and equal to 1·268.

Strychnine.—Two samples of different character were recrystallised from alcohol, and dissolved both in 80° alcohol and in chloroform. Notwithstanding considerable differences in the rotative power of the two samples in both solvents, the dispersive power was constant and equal to 1·313.

Camphor.—This substance was recrystallised from alcohol and fused. It was dissolved in alcohol of various strengths, in chloroform, and in dry ether. The rotative power varies with the nature of the solvent; its dispersive power is sensibly constant. In alcoholic solution, the rotative power increases with concentration of the alcohol, In dry ether, the rotative power does not vary with the concentration of the solution. In chloroform, as well as in alcohol, the dispersive power remains constant, notwithstanding that the rotative power increases with the concentration.

Cholesterin.—This was observed in ether and chloroform. Its dispersive power averages 1·323. It does not vary, like the rotative power, with the nature of the solvent.

Essence of Térébenthine.—A lævorotatory sample gave—

$$[\alpha]_D = -30{\cdot}46,\ [\alpha]_C = -28{\cdot}57, \text{ and } [\alpha]_D/[\alpha]_C = 1{\cdot}241.$$

The results obtained with the foregoing substances show that the dispersive power remains constant whatever be the concentration of the solution; that the dispersive power of those substances whose rotative power varies with the temperature, remains constant all through that variation; that for the same substance it scarcely varies with the nature of the solvent; that each substance has its own proper dispersive power which seems to bear no relation to the chemical constitution of the substance, although it may be noted that the sugars have all the same value. J. T.

Distribution of Electromotive Force in the Cells of Batteries. By J. Miesler (*Monatsh.*, 8, 626—631).—The author has extended the work of Moser (this vol., p. 209) to the batteries of Grove, Bunsen, Grenet, Smee, Lalande, and Leclanché. In every case, the total electromotive force of the battery under examination was found to be equal to the sum of the electromotive forces between the different parts of the cell. G. T. M.

Electrochemical Studies. By W. OSTWALD (*Zeit. physikal. Chem.*, 1, 74—86 and 97—109).—From his former experiments (*J. pr. Chem.*, 1884—1886), the author has drawn the conclusion that the molecular conductivity increases for monobasic acids with increasing dilution, tending to a maximum value which it was thought would prove to be the same for all acids. On careful repetition of these experiments, the latter view is found to be incorrect, as the maxima observed for a dilution of 1024 litres differ for 15 different acids by as much as 12 per cent. That this difference does not affect the proportionality between the maximum conductivity and the rate of chemical action of these acids is proved by experiment, the latter being in fact proportional to the relative observed maximum conductivity. A difficulty, however, obviously arises in determining the value of this maximum for feeble acids of low conductivity.

To overcome this, Kohlrausch's law that the conductivity of a neutral salt may be represented as a sum of two constants, one of which depends on the nature of the acid and the other on that of the base, is resorted to. It is shown by the determination of the conductivities of a number of sodium salts of acids of known conductivity that a constant difference exists between the two. The same holds good for lithium and potassium salts, which also differ in conductivity from the sodium salts by a constant fixed quantity. The molecular conductivities of different salts having the same base, differ very largely amongst themselves, and altogether contradict the opinion of Arrhenius and Bouty that the molecular conductivities of dilute salt solutions are the same. The numbers prove, however, that it is possible to represent the conductivity of an acid by that of one of its salts, plus some constant. The determination of these constants is reserved for a future paper.

Another interesting result is that there is an almost constant increase in the molecular conductivity of the sodium salts of the monobasic acids, with an increase in the dilution of from 32 to 1024 litres, varying between 10 and 13 units. The poorer conductors give the smaller value, so that the increase appears to depend partly on the conductivity. For bibasic acids it has about double the above value, and is nearly three times as great for tribasic. Polyvalent bases act similarly to polyvalent acids although not quite so regularly. It would seem, in fact, that if m is the molecular conductivity, and v the dilution, dm/dv is of the form $n_1 \times n_3 \times$ const., where n_1 is the valency of the acid, and n_2 that of the base. According to this mode of testing, dithionic acid appears to be truly bibasic. H. C.

Pyrometer. By J. MENSCHING and V. MEYER (*Zeit. physikal. Chem.*, 1, 145—158).—The advantage of the instrument presently to be described is that it affords a quick as well as an exact measurement of temperature. The principle of the method is to determine the temperature from the measurement of the volumes of gas contained in the instrument at the temperature of the laboratory and at the higher temperature that is required. Part of the instrument is at a low temperature, but error from this cause is obviated by means of a compensator.

The instrument consists of a vapour-density vessel, a platinum cylinder 200 mm. high and 36 mm. in diameter. To the middle of one end of the cylinder is connected a platinum tube 350 mm. long and 4 mm. in diameter. Close by the side of this tube runs a platinum capillary tube with very thick walls, which passes through the circular end of the vapour-density vessel and goes down to within 3 mm. of the bottom. The end of the capillary tube is bent round through a right angle. The compensator is composed of a platinum tube connected at one extremity with a capillary tube, so that it is of exactly the same shape and size as the part of the instrument outside the cylinder. The instrument was heated by Perrot's gas-oven, by means of which a temperature of about 1500° can be produced.

Incandescent platinum, as Deville and Troost have shown, is permeable by hydrogen but not by air. The platinum cylinder was therefore surrounded by a Berlin porcelain tube which is impermeable to all gases.

In making an experiment, the platinum cylinder was filled with nitrogen by an india-rubber tube attached to the capillary tube, and communicating with a series of drying tubes connected with a gasometer. The quantities of gas contained in the whole instrument and the compensator at the higher temperature T were measured, and the difference reduced to volume at temperature 0° and normal pressure. Then V being a similar quantity for the temperature of the laboratory, T is given by—

$$T = (V - v)/(V\alpha - V\gamma),$$

when α, γ are the coefficients of cubical expansion of platinum and nitrogen. C. S.

Specific Heat of Tellurium. By C. Fabre (*Compt. rend.*, **105**, 1249—1251).—Tellurium was precipitated by means of sulphurous acid, washed with water saturated with nitrogen, and dried in a current of nitrogen. The mean of three determinations of the specific heat is 0·05252. The same tellurium was volatilised in a current of sulphurous anhydride, and was thus obtained as a black sublimate with a crystalline fracture, different in appearance from the product obtained by distillation in hydrogen. Determinations of the specific heat gave 0·05182.

Crystallised tellurium was prepared by the decomposition of alkaline tellurides, washed with water saturated with nitrogen, distilled in a current of hydrogen, fused, and allowed to cool slowly. It had a crystalline fracture. Two determinations of the specific heat gave as the mean 0·048315.

From these results, it follows that the various forms of tellurium have sensibly the same specific heats at temperatures near 100°.

Possibly differences may appear at higher temperatures, and especially near the point of transformation of amorphous tellurium into the crystalline variety. C. H. B.

Constancy in the Heat produced by the Reaction of certain Salts on each other. By S. U. PICKERING (*Chem. News*, **57**, 75—77). —The author shows that the constancy in the heat evolved in the reaction of silver nitrate on metallic chlorides in solution, observed by Richards (*Chem. News*, **57**, 16), is an inevitable consequence of the heat of neutralisation of hydrochloric and nitric acids being independent of the nature of the alkali, the number 16165 cal. being merely the heat of precipitation of silver chloride. Similarly, the heat measured by Fay on adding barium chloride to sulphates is the heat of precipitation of barium sulphate, 5580 cal. In this case, however, it is constant only when dyad metals are concerned, since it is only with these that the difference between the heat of neutralisation of the hydrate with sulphuric and hydrochloric acids is a constant quantity. The quantities determined by Fay have already been determined by Thomsen. S. U. P.

Heat Equivalents of Benzoyl Compounds. By F. STOHMANN, P. RODATZ, and W. HERZBERG (*J. pr. Chem.* [2], **36**, 353—370).—The authors, continuing their previous work (Abstr., 1887, 878), have determined the heat of combustion (in free oxygen) of the following benzoyl-compounds:—

	Heat equiv. per gram-mol.	Heat of formation.
Glyceryl benzoate, $C_3H_5(C_7H_5O_2)_3$	2720536	225464
Mannityl benzoate, $C_6H_8(C_7H_5O_2)_6$	5361915	461085
Benzophenone, $COPh_2$	1557556	9444
Acetophenone, COMePh (solid)	1001400	26600
" " (liquid)	1003440	24560
Methyl salicylate, OH·C_6H_4·COOMe	898776	129224
Ethyl " OH·C_6H_4·COOEt	1051748	139252
Propyl " OH·C_6H_4·COOPr	1206120	147880
Isobutyl " OH·C_6H_4·COOBu$^\beta$	1366270	150730
Methyl parahydroxybenzoate, OH·C_6H_4·COOMe (solid)	889200	138800
Ethyl parahydroxybenzoate, OH·C_6H_4·COOEt (solid)	1043310	147690
Propyl " OH·C_6H_4·COOPr (solid)	1201117	—

Comparing the differences of the heat equivalents of the benzoates, salicylates, and parahydroxybenzoates, the authors calculate the heat of combustion for salicylic acid to be 723600 cal., that of parahydroxybenzoic acid 715839 cal. Thus, whilst the substitution of a hydrogen in benzoic acid to form salicylic acid decreases the heat-value 46833 cal., a similar substitution to form the para-acid decreases it 54628. The latter number is very close to that found in the formation of phenols from benzene, and it therefore appears that the para-acid more closely corresponds with the phenols than the ortho-acid does.

Glyceryl benzoate was prepared by the action of glycerol and soda on benzoic chloride. It forms long, silky needles melting at 72·4°. *Mannityl benzoate* forms colourless scales melting at 124—125°.

L. T. T.

Boiling Points and Specific Volumes of the Normal Fatty Ethers. By P. Dobriner (*Annalen*, **243**, 1—22).—The author's experiments lead him to the following results. In the case of metameric ethers, the boiling point falls as the difference in the number of carbon-atoms in the two alcohol radicles diminishes. Methyl ethers have the highest boiling points. In a series of homologous ethers containing one alcohol radicle in common, the difference between the boiling points diminishes as the carbon-atoms increase in number. Methyl ethers form an exception to this rule, as the difference between the boiling points of the methyl and ethyl ethers in such an homologous series is smaller than the difference between the ethyl and propyl ethers.

The boiling points of amyl and hexyl ethers can be calculated approximately, as the difference between the boiling points of homologous amyl and hexyl ethers is equal to one-third of the difference between butyl and heptyl ethers. The difference between butyl and amyl ethers is a little larger, and the difference between hexyl and heptyl ethers is a little less.

The difference between the boiling points of methyl and ethyl compounds is smaller than the difference between ethyl and propyl compounds when the alcohol radicles are directly attached to an oxygen-atom (for instance, in the case of the methyl, ethyl, and propyl salts of the adipic acids), but the case is reversed if the alcohol radicles are directly united to carbon-atoms.

Specific Gravity.—In the case of metameric ethers, the highest specific gravity is exhibited by the ether with the highest boiling point, and the lowest specific gravity by that of the lowest boiling point. In an homologous series, the specific gravity at 0° increases with the carbon-atom, but the specific gravity at the boiling point diminishes as the compounds increase in carbon.

Specific Volume.—The specific volume of an ether is approximately identical with that of an ethereal salt, the radicles of which contain the same number of carbon atoms. The specific volumes of the ethers are larger than the specific volumes of the metameric alcohols. In a series of metameric ethers, the methyl ether has the smallest coefficient of expansion.

W. C. W.

Specific Volumes of Normal Alcoholic Iodides. By P. Dobriner (*Annalen*, **243**, 23—31).—The specific volumes of the following iodides were determined:—

CH_3I,	64·1	$C_5H_{11}I$,	151·2
C_2H_5I,	85·7	$C_6H_{13}I$,	175·5
C_3H_7I,	106·8	$C_7H_{15}I$,	198·6
C_4H_9I,	128·5		

The specific volume of an iodide $C_nH_{2n+1}I$ is the same as that of an acid of the formula $C_nH_{2n+1}\cdot COOH$. W. C. W.

Boiling Points and Specific Volumes of Phenols and their Ethers. By J. Pinette (*Annalen*, **243**, 32—63).—In homologous ethers of the same phenol, the difference in the boiling points of the methyl and ethyl ethers is about 5° less than the difference between those of the ethyl and propyl ethers. In ascending the series from the ethyl ethers, the difference gradually diminishes. The difference between phenol and thymol ethers of the same alcohol radicle decreases with an increase of carbon in the alcohol radicle. Meta- and para-cresol have almost the same boiling point, this is also true of their metameric ethers. Orthocresol boils about 11°, and its ethers about 6° lower than the corresponding meta- and para-compounds. The boiling points of propyl, butyl, and octyl phenyl ethers are almost identical with the boiling points of the metameric ethers of meta- and para-cresol, and are higher than the orthocresol and thymol-derivatives.

The difference between the boiling point of a phenol and its methylic ether decreases with the increasing molecular weight of the phenol.

Specific Volume.—Phenols have a smaller specific volume than the metameric ethers. The specific volumes of phenol and its ethers coincide with those of butyl alcohol and its ethers. Meta- and para-cresols and their ethers have approximately the same specific volumes; they are about 1 per cent. higher than the corresponding orthocresol-derivatives. The specific volumes of the thymol ethers are relatively small.

The author obtains the following values for the specific volumes of the isomeric xylenes:—

	Ortho.	Meta.	Para.
	137·6	139·75	139·9
Schiff found	139·9	139·7	140·2

W. C. W.

Boiling Points and Specific Volumes. By W. Lossen (*Annalen*, **243**, 64—103).—The author has compared the boiling points of a large number of organic compounds, and agrees with Dobriner (preceding page) that in an homologous series, the first difference (that is the difference between the boiling points of methyl and ethyl compounds) is less than the second (namely, between ethyl and propyl) when the alcohol radicle is attached to the rest of the molecule by an oxygen-atom. When the radicle is attached to a carbon-atom, the reverse is true in the majority of cases. In many cases, the first and second differences are equal, and in a few cases the first difference is a little less than the second.

The author agrees with Horstmann (Abstr., 1886, 759) that a comparison of molecular volumes determined at the same temperature possesses many advantages not shared by specific volume determinations at the boiling point. W. C. W.

Estimation of Vapour-densities. By C. Schall (*Ber.*, **21**, 100—101).—Further modifications in the apparatus lately described by the author (Abstr., 1887, 695, 882). J. W. L.

Determination of Vapour-density at Low Pressure. By H. Malfatti and P. Schoop (*Zeit. physikal. Chem.*, 1, 159—164).—In spite of the many modifications of methods of measuring vapour-density, there is not at present a convenient method when the tension is small. Hofmann's method requires for small tensions a cumbrous apparatus, whilst in Habermann-Dumas' method there is the objection of the additional determination of the weight of the vapour.

A tubular glass vessel of 100 c.c. capacity closed at one end is carefully cleaned and dried. Inside the tube is placed a short barometer tube. The substance is weighed in a small glass sphere having two sides drawn out into fine tubes; one capillary tube is stopped with alloy, and the other hermetically sealed after the introduction of the substance. The end of the glass vessel is drawn out into a capillary tube and the air is exhausted from the vessel; when the levels of the arms of the barometer tube remain unaltered the vessel is hermetically sealed. It is next immersed in a bath of known temperature, and the difference of level of the arms of the barometer is read off by a millimetre scale, so that the pressure is known. The vessel is immersed in water and the capillary point broken off. The vessel when filled is weighed. Thus, having measured the volume of a given length of the barometer tube, we have sufficient data to determine the vapour-density.

In order that the barometer may contain no moisture, it is constructed as follows :—A tube is bent into the form of a double U-tube, and one end is passed through a cork inserted in the neck of a fractional distillation flask which contains a small quantity of mercury. The flask is inclined, so that the end does not touch the mercury, and heated while dry air is drawn through the tube. When the flask is placed upright, the tube is immediately filled with mercury.

The proper quantity of substance to be placed in the sphere is determined by a preliminary calculation. For higher temperatures, the barometer is filled with an alloy of 3 parts lead and 1 part tin, which does not stick to the tube and has no perceptible tension.

For higher temperatures, the author also shows that a modification of L. Meyer's apparatus (*Ann. Phys. Chem.* [2], 1880, 550) can be employed. C. S.

Viscosity of Dilute Aqueous Solutions. By S. Arrhenius (*Zeit. physikal. Chem.*, 1, 285—298).—The solution is contained in a glass sphere of volume 0·9846 c.c., and is allowed to flow vertically through a fine capillary tube, the bore of which suddenly enlarges at its lower end, so that the velocity of efflux is negligible. The flow of liquid may be started by turning on a tap connected with the upper part of the sphere. The sphere and the capillary tube connected to it are immersed in a water-bath so that the solution may be kept at a known temperature. Since the liquid escapes with a very small velocity, the work done by the solution in falling through the height of the capillary tube will be entirely spent in overcoming the resistance due to viscosity, provided no energy is consumed in setting up vortex-motion as the liquid passes from the capillary tube into its enlarged end. In any case, the energy so spent will be less than if all the kinetic energy of the liquid passing into the enlargement were employed in setting up vortex-motion. But on this hypothesis the energy spent may be calculated by a formula given by Hagenbach (*Ann. Phys. Chem.*, **109**, 385), and was found to be negligible with the dimensions of the apparatus used by the author. Thus a correction, which has been calculated by various experimenters on hypotheses never completely satisfied, is entirely avoided. By placing the capillary tube vertical, the small particles which are seen to form are carried away and not left adhering to the sides of the tube. Hence the coefficient of relative viscosity, η, will be given by $\eta = (st)/(ST)$, when s is the specific gravity of the solution, t the time of efflux of the volume contained in the sphere, and S, T similar quantities for water.

The results of numerous experiments show that the relative viscosity of a dilute aqueous solution of two different substances is equal to $A^x B^y$, where x, y are the volume percentages of the two substances, and A and B two functions of the temperature which remain constant for the same temperature and the same substance. There does not appear to be any connection between A and the viscosity of the corresponding substance. The constant A diminishes as the temperature increases in the case of non-conductors, so that the values of the relative viscosity tend to a common limit, unity. The viscosity of water ~~is~~ increased by the addition of a small quantity of a non-conductor. Those normal solutions which have greater conductivity have in general less relative viscosity, but there does not seem to be any simple law connecting conductivity and viscosity. C. S.

Dissociation of Hydrated Salts. By P. C. F. FROWEIN (*Zeit. physikal. Chem.*, **1**, 5—14 and 362—364).—The relation which must exist between the heat of combination of the water in hydrated salts and the maximum vapour-tension has been thermodynamically calculated, but hitherto has not been experimentally established in a satisfactory manner. This is the aim, therefore, the author has in view.

The thermodynamical relation given by Van't Hoff, $d\,.\,lK/dT = q/2T^2$, is transformed, in order to be applicable to calorimetric work, into $d\,.\,lF/dT = Q/2T^2$, where T is the absolute temperature, Q the amount of heat evolved by the absorption of 18 kilos. OH_2 by the dehydrated salt, and F the ratio of the maximum tensions of salt and water. By integration of the above on the assumption that Q remains constant between small limits of temperature—

$$Q = \frac{2T_1T_2}{T_1 - T_2}\, l\, \frac{F_1}{F_2}.$$

This equation does not, however, give numbers agreeing with Thomsen's observed values for the heat of combination in the cases of $CuSO_4 + 5OH_2$; $BaCl_2 + 2OH_2$; $SrCl_2 + 6OH_2$; $MgSO_4 + 7OH_2$, and $ZnSO_4 + 7OH_2$, if the values for F_1F_2 are calculated from the numbers given by Pareau and Wiedemann for the vapour-tensions.

Attributing this to errors in the vapour-tension determinations, arising partly from the very small differences in pressure which have to be observed, the author has redetermined these by means of an apparatus in which olive oil is used in the manometer in place of mercury. The numbers thus obtained for F_1F_2 give values of Q which agree well with those observed by Thomsen for all the before-mentioned salts, with the exception of $SrCl_2 + 6OH_2$. The tension of $Na_2HPO_4 + 12OH_2$ has also been redetermined, and the calculated value for Q brought into agreement with the observed, a result which the former determinations by Debray and Müller-Erzbach had not rendered possible. H. C.

Nature of Chemical Affinity. By W. OSTWALD (*Zeit. physikal. Chem.*, 1, 61—62).—In a former paper (Abstr., 1886, 294), the author has pointed out that chemical affinity depends not only on the nature and the relative distance of the atoms from one another, but also on the direction in which it acts. The difference in the molecular conductivities of the two nitrosalicylic acids, [$COOH : OH : NO_2$ = 1 : 2 : 3 and 1 : 2 : 5], is here offered as proof that although in each the relative positions of the NO_2 and OH to the COOH-group is the same, yet the former acid is the stronger of the two, the closer grouping of the radicles being more favourable to their combined action. H. C.

Thermodynamical Expression of the Influence of Temperature on the Rate of Chemical Change. By F. URECH (*Ber.*, 21, 56).—A continuation of the author's investigations (Abstr., 1887, 768). Instead of Van't Hoff's expression, $\log c = -A/T + BT + C$, the equation $\log c = -A'/T + B'$, corresponding with the thermodynamical formula $\log c = -q/RT + B'$, has been applied, and is found to give results agreeing generally with the author's observed values for the rates of inversion of saccharose with hydrochloric acid of different strengths. H. C.

Action of Sulphurous Acid on Periodic Acid and Rate of the Change. By F. SELMONS (*Ber.*, 21, 230—241).—The action of sulphurous acid on periodic acid takes place for all proportions of the two acids, the products varying, however, with the amounts employed. A separation of iodine takes place only within the limits represented by the equations—

$$4H_2SO_3 + HIO_4 = 4H_2SO_4 + HI$$
$$4H_2SO_3 + 4HIO_4 = 4H_2SO_4 + 4HIO_3,$$

namely, when more than one and less than 4 mols. HIO_4 enter into reaction with 4 mols. H_2SO_3, the production of iodine being in fact due to the action of the hydriodic on the iodic acid.

With dilute solutions, the rate of change of the reactions involving the production of iodine from sulphurous and periodic acids can be measured, using starch solution as an indicator. This reaction is similar to that studied by Landolt (Abstr., 1886, 658) on the action of sulphurous acid on iodic acid, and depends on the concentration of the solutions when the proportion between the two acids is kept constant, on the molecular weights for unit concentration, and on the temperature. If C_s is the concentration of the sulphurous, C_p that of the periodic acid, then the time $t = k_1/(C_sC_p)^z$, where calculated from two consecutive observations, $z = \frac{\log t - \log t_1}{\log (C_sC_p)_1 - \log (C_sC_p)}$. If the sulphurous acid be kept constant in amount, and the periodic acid allowed to vary, $t = k/C_p^y$, where k is constant and y calculated from two consecutive observation $\frac{\log t' - \log t''}{\log C''_p - \log C'_p}$. H. C.

Influence of Molecular Contiguity on the Chemical Equilibrium of Homogeneous Gaseous Systems. By SARRAU and VIEILLE (*Compt. rend.*, **105**, 1222—1224).—The combustion of organic compounds which do not contain sufficient oxygen for complete oxidation results in the production of a condition of equilibrium between the gaseous products, some of which are completely oxidised, as carbonic anhydride and water, whilst in others, such as carbonic oxide, hydrogen, and methane, oxidation is incomplete. Experiment shows that the conditions of final equilibrium change with an increase in the weight of substance exploded in the same space, that is to say, with an increase in the pressure produced by the products. Two principal reactions are concerned in the progressive alteration of equilibrium. The first $CO + H_2O = CO_2 + H_2$, usually occurs; the second, $2CO + 2H_2O = CO_2 + CH_4$, takes place when the first has reduced the proportion of water vapour and increased the proportion of free hydrogen to a certain extent, or when the explosive contains so little oxygen that water is formed in relatively very small quantity. The first reaction was observed to take place by Noble and Abel in their experiments with gunpowder. The authors find that it also takes place in the explosion of cotton powder and of picrates. The results obtained with cotton powder, $C_{24}H_{29}N_{11}O_{42}$, are as follows:—

Density of gas.		Methane.
0·010	$33CO + 15CO_2 + 8H_2 + 11N_2 + 21H_2O$	0·00
0·023	$30CO + 18CO_2 + 11H_2 + 11N_2 + 18H_2O$	0·00
0·200	$27CO + 21CO_2 + 14H_2 + 11N_2 + 15H_2O$	0·006
0·300	$26CO + 22CO_2 + 15H_2 + 11N_2 + 14H_2O$	0·016

The temperature of final equilibrium is about 3000°, the pressure varying between 100 and 4000 atmospheres. The formation of methane, which occurs only to a very limited extent in the case of cotton powder, becomes more marked with such compounds as the lower nitrated derivatives, picrates, and picric acid. The results with the last compound were as follows:—

Density of gas.	
0·10	$11CO_2 + 84CO + 24N_2 + CH_4 + 16H_2 + 6H_2O$
0·30	$20CO_2 + 69CO + 24N_2 + 7CH_4 + 7H_2 + 3H_2O$
0·50	$25CO_2 + 61CO + 24N_2 + 9\frac{1}{2}CH_4 + 4H_2 + H_2O + \frac{1}{2}C$.

The pressures varied from 1000 to 7500 atmos. The reactions which tend to reduce the proportion of carbonic oxide are exothermic.

In the case of the first reaction, the development of heat is not great, and there is no alteration in the volume of the gas; but in the second case there is a considerable development of heat, and the volume of the gases taking part in the change is reduced to one-half. The alterations in the conditions of equilibrium tend towards the development of the maximum quantity of heat, and the two reactions concur in making the pressure increase in a greater ratio than the weight of the explosive charge. C. H. B.

Influence of Neutral Salts on the Rate of Hydrolysis of Ethyl Acetate. By S. Arrhenius (*Zeit. physikal. Chem.*, 1, 110—133).—In Warder and Reicher's equation for the rate of saponification, $-\frac{dC}{dt} = kCC_1$, where t is the time, C the concentration of the base, and C_1 that of the salt, k is a quantity which the author proposes to call the specific rate of saponification. This quantity is independent of the amounts of base and salt which act on one another, but most probably varies for different concentrations. In the present case, the influence of the presence of neutral salts on k was studied. This influence is as a rule small, and k remains nearly constant; salts of the halogens and nitrates lower, whilst sulphates and hyposulphites raise the value of k. The influence of potassium iodide is greater than that of potassium bromide, which is greater than that of potassium chloride, the three being very nearly in the ratio 3 : 2 : 1.

Quite abnormal is the influence of ammonia and ammonium salts, the action being very great and varying very distinctly with the amount of salt in solution. k in fact here depends on the amount of dissolved salt, S, according to the equation $k = \frac{A}{1 + aS + bS^2}$

The rate of hydrolysis is practically in all cases proportional to the conductivity. The low conductivity of a weak base such as ammonia, on which other dissolved electrolytes can exercise such a large relative influence, probably explains its abnormal behaviour.

H. C.

Formation and Decomposition of Ethereal Salts: Decomposition of Liquid Tertiary Amyl Acetate. By D. Konowaloff (*Zeit. physikal. Chem.*, 1, 63—67).—Menschutkin (Abstr., 1883, 178, 309) has observed that the rate of decomposition of liquid tertiary amyl acetate at 180° increases until about 50 per cent. of the acetate employed is decomposed, then diminishes, and finally ceases when the decomposition has reached 97·42 per cent. The author shows that the cause of this is the action of the liberated acetic acid on the acetate, and finds that the addition of acetic acid brings about the decomposition of the acetate. By heating amyl acetate with varying amounts of acetic acid for one hour at 159°, he shows that the amount decomposed is dependent on the amount of acetic acid added. This is expressed by the equation $dx/dt = k\ (100 - x)\ (x + 2\frac{1}{8}p)$, where x is the percentage of acetate decomposed in the time t, p the quantity of acetic acid added, $2\frac{1}{8}$ the ratio of the molecular weights of the acetate and acetic acid, and k a constant. All other acids have an action similar to this of acetic acid although in different degree, propionic and butyric acids being far less active.

The action of the haloïd hydrogen acids was also studied, but in these cases the gaseous acid was passed into the liquid acetate at the ordinary temperature. The action is violent, a considerable development of heat takes place, and a tertiary amyl haloïd salt and acetic acid are formed. In the action of hydrogen chloride two stages may be distinguished, the acetate being first decomposed into amylene and acetic acid, and the amylene then combining with the hydrogen chloride. This reaction the author proposes to employ to determine the heat-change represented by $C_5H_{11}\cdot C_2H_3O_2 = C_5H_{10} + C_2H_4O_2$. The comparative ease with which the halogen acids act on tertiary amyl acetate explains the formation of amyl chloride instead of acetate when dimethyl ethyl carbinol is treated with acetic chloride.

H. C.

Chemical Decomposition produced by Pressure. By W. Spring and J. H. van't Hoff (*Zeit. physikal. Chem.*, 1, 227—230).—The results of numerous experiments show that in many cases substances which exert no action on each other at atmospheric pressure under ordinary circumstances, can be made to combine more or less completely if they are subjected to a pressure sufficient to cause a perceptible condensation. The researches hitherto made relate to compounds, the volume of which is smaller than that of their constituents. It is therefore a question of some interest and importance to examine whether the temperature of conversion can be lowered in the case of copper calcium acetate, for which the volume is greater than that of its constituents.

In the first experiment the acetate finely powdered at a temperature of 16° was submitted to a pressure of 6000 atmospheres. The powder was thus reduced to a crystalline mass resembling marble, but presenting no sign of chemical decomposition. Next a screw press (*Bull. Acc. Belg.*, **49**, 344) was employed; at a temperature of 40° there were very marked results; three-fourths of the mass being liquefied. On removing the pressure, it became solid again, but the sides of the containing vessel were covered with a coating of copper, and it was possible to pick small leaves of copper out of the mass. The dark blue of the acetate had changed for the most part to green interspersed with white points, showing that the mass had been decomposed into acetate of copper and acetate of calcium. The result was entirely due to the change of volume, since the thermal effect of compression was less than a rise of 1°. When the temperature was raised to 50°, the piston sank without resistance through the mass. The first experiment, which had given a nugatory result, was now repeated in order to discover whether sufficient pressure had been used, or the result had escaped observation. A press worked by a lever was used, and this time it was found that the piston sank 1·25 mm. in an hour, or, roughly, that the whole could be decomposed in about 110 hours. Lastly, potassium sulphate under the same conditions gave no perceptible diminution of volume. Thus, the higher the pressure and temperature, the more quickly is the acetate decomposed. Since the progress of chemical action depends on the time, it seems that it is not sufficient to say that the molecules of a substance assume the arrangement which corresponds with the given volume directly it is reached, for a substance can be compressed without altering its state, if the pressure does not last too long. C. S.

Crystallisation of Mixtures. By O. LEHMANN (*Zeit. physikal. Chem.*, 1, 15—26 and 49—60).—The author discusses the different cases in which mixed crystals have been formed, and the possibility of obtaining such from non-isomorphous forms. He repeats the experiments of Herrmann (Abstr., 1886, 972), on the crystallisation of ethyl quinonedihydroparadicarboxylate with ethyl succinosuccinate with similar results. He also investigates the mixed crystals of ethyl dihydroxyquinoneparadicarboxylate with ethyl tetrahydroxybenzeneparadicarboxylate, and of each of these with each of the two foregoing. These substances, although having a somewhat analogous chemical constitution, differ pretty widely in crystalline form. They give, however, well-defined mixed crystals of form and colour intermediate between those of the two substances of which they are formed.

H. C.

Constitution of Solutions. By F. RÜDORFF (*Ber.*, 21, 4—11).—Numerous experimenters have found that the solution of a double salt diffuses as if it were a solution of a mixture of its component parts; for this and other reasons, it is generally stated that double salts do not exist as such in solution.

On dialysing solutions of the following double salts, $K_2SO_4,NiSO_4 + 6H_2O$; $K_2SO_4,MnSO_4 + 6H_2O$; $(NH_4)_2SO_4,MnSO_4 + 6H_2O$; $K_2SO_4,Cr_2(SO_4)_3 + 24H_2O$; $2KCl,CuCl_2 + 2H_2O$; $2NH_4Cl,CuCl_2 + 2H_2O$; $2KCl,ZnCl_2 + H_2O$; $KCl,MgCl_2 + 6H_2O$; $2NaCl,CdCl_2 + 3H_2O$; $BaCl_2,CdCl_2 + 4H_2O$, it was found that the ratio of the metals in the dialysate was entirely different from that in the original liquid; the component parts, therefore, do not form a molecular compound, but exist in solution independently of each other. On the other hand, the following double salts, $KCN,AgCN$; $2KCN,Hg(CN)_2$; $2KCN,Cd(CN)_2$; $2KCN,Ni(CN)_2$; $6KCN,Cu_2(CN)_2$; $2NaCl,PtCl_4 + 6H_2O$; $3Na_2C_2O_4,Fe_2(C_2O_4)_3 + 6H_2O$; $3K_2C_2O_4,Fe_2(C_2O_4)_3 + H_2O$; $3K_2C_2O_4,Cr_2(C_2O_4)_3 + 6H_2O$; are not decomposed, but must exist in solution and diffuse as such, inasmuch as the ratio of the metals is found to be the same in the dialysate as in the original liquid.

Several simultaneous experiments were made with each salt, and a membrane prepared from the cuticle of the cæcum of an ox was found to be most suitable, a parchment membrane not being sufficiently homogeneous, F. S. K.

Absorption of Gases by Petroleum. By S. GNIEWOSZ and A. WALFISZ (*Zeit. physikal. Chem.*, 1, 70—72).—The statement that a layer of petroleum will protect an aqueous solution from the action of the air has led the authors to examine the absorption of oxygen and other gases by Russian petroleum. The following table contains the results :—

	Absorption coefficients for petroleum at		Ratio.	Water at 20°.
	20°.	10°.		
H_2	0·0582	0·0652	1·12	0·0193
N_2	0·117	0·135	1·15	0·0140
O_2	0·202	0·229	1·13	0·0284
N_2O	2·11	2·49	1·18	0·670
C_2H_4	0·142	0·164	1·15	0·149
CO_2..............	1·17	1·31	1·12	0·901
CO..............	0·123	0·134	1·09	0·0231
CH_4	0·131	0·144	1·10	0·0350

The ratio is given on account of E. Wiedemann's statement that the changes which the absorption coefficients of different gases undergo with change of temperature is about the same for all gases; the values for water are given for the sake of comparison. It will be seen that the absorption of oxygen is greater for petroleum than for water, so that the protective action above spoken of must be a doubtful one.

H. C.

Lecture Experiments with Nitrogen Chloride. By V. MEYER (*Ber.*, **21**, 26—28).—An experiment is described by which the explosion of nitrogen chloride can be shown, without danger, by allowing turpentine to come into contact with a few drops of the chloride swimming on the surface of the electrolysed ammonium chloride solution contained in an inverted flask, the whole apparatus being placed under a thick glass case.

F. S. K.

Inorganic Chemistry.

Specific Gravity of Sulphuric Acid Solutions. By D. MENDELÉEFF (*Zeit. physikal. Chem.*, **1**, 273—234).—The composition of the solutions is expressible by the formula $H_2SO_4 + mH_2O$; p denotes the percentage of H_2SO_4 in the solution, taking $S = 32$, $O = 16$, and s is its specific gravity. A table of the value of s derived from the researches of seven experimenters is given for different values of m. Plotting a curve, abscissæ representing the values of p, ordinates those of ds/dp, it appears that the curve consists of a number of straight lines, the discontinuities corresponding with the known hydrates. Since ds/dp is a linear function of p, an integration shows that s is a rational function of p of the second degree, the constants remaining unchanged between two consecutive discontinuities or two consecutive hydrates.

Thus for the values $m = 0, 1, 2, 6, 150$, there are discontinuities in the values of ds/dp, the first being the most considerable. The data given are not sufficient to determine the positions of the discontinuities for $m = 6$ and $m = 150$ with accuracy. Formulæ are given for ds/dp and s in terms of p for the intervals through which these quantities are continuous, and it is shown that ds/dp = a linear function of p is probably not an approximation but an exact law. The same law obtains in the case of alcohol solutions. C. S.

Pyrosulphites. By W. MEYSZTOWICZ (*Zeit. physikal. Chem.*, **1**, 73).—The failure of an attempt to prepare pyrosulphites of polyvalent metals leads the author to draw an analogy between pyrosulphurous and dichromic acids, concluding that in each the position of the hydrogen-atoms is such that they cannot be simultaneously replaced by a bivalent element. H. C.

Action of Water on Lead Pipes. By E. REICHARDT (*Arch. Pharm.* [3], **25**, 858—877).—In the vast majority of cases where lead pipes are used for domestic water supply, no injurious results follow, but in some few cases highly dangerous lead poisoning has been experienced. When lead is alternately in contact with air and water, it is rapidly attacked, and the water becomes impregnated. This solvent action is doubtless due to the oxygen of the air; but when the lead is always in contact with water only, whether under pressure or not, the presence or absence of dissolved oxygen appears to have no effect on the amount of lead dissolved. The author examined two different water supplies which caused lead poisoning where lead service pipes were employed, and compared these with several other waters which did not take up lead under similar conditions. The contaminated waters were found to contain free carbonic anhydride, that is more than was required to form bicarbonates with the bases present as carbonates, and when this free anhydride was expelled, as by boiling, or neutralised, the water no longer acted on lead. The uncontaminated waters did not contain this excess of anhydride, but on adding excess of the anhydride the waters became capable of dissolving lead (compare (Müller, this vol., p. 225). J. T.

Tungsten Compounds. By W. FEIT (*Ber.*, **21**, 133—137).—By the reduction of a fused mixture of sodium and potassium tungstates with tin, the author obtains the compounds $3K_2W_4O_{12} + 2Na_2W_3O_9$ and $5K_2W_4O_{12} + 2Na_4W_5O_{15}$, prepared by v. Knorre (Abstr., 1883, 650, 651), and also a compound which probably has the formula $K_2W_4O_{12} + Na_2W_5O_{15}$. The author has endeavoured to prepare corresponding compounds of lithium. By reducing a fused mixture of sodium tungstate and lithium tungstate with tin, three compounds are obtained, a deep blue lithium compound (probably $Li_2W_5O_{15}$) and two sodium compounds, one of which seems to be the compound $Na_6W_6O_{18}$. A homogeneous product, $Li_2W_5O_{15} + 3K_2W_4O_{12}$, crystallising in violet needles, is obtained by reducing a mixture of potassic tungstate (one mol.), and lithium tungstate (one mol.). As the proportion of base and acid (3 : 7 or 5 : 12) in the paratungstates of the light metals can scarcely be proved by analysis, the difference being too small, the author intends to prepare the salts of some metals of a high atomic weight. J. W. L.

Boiling Point and Molecular Formula of Stannous Chloride. By H. Biltz and V. Meyer (*Ber.*, **21**, 22—24).—The boiling point of stannous chloride is found to be 606·1°, as a mean of two series of experiments.

The vapour-density of this salt diminishes only very gradually with an increase of temperature, so that it must be heated hundreds of degrees above its boiling point in order to obtain numbers agreeing with the molecular formula $SnCl_2$. The determinations made at temperatures less than 100° above the boiling point show that the view of V. and C. Meyer, that at low temperatures the molecular formula is Sn_2Cl_4, cannot be upheld; for although at relatively low temperatures values are obtained which are greater than those corresponding to $SnCl_2$, no constant results could be obtained which would lead to the doubled formula. F. S. K.

New Source of Germanium. By G. Krüss (*Ber.*, **21**, 131—133).—The author finds that germanium is contained in euxenite to the amount of 0·1 per cent., and that it replaces titanium in this mineral. He intends to examine other minerals, such as rutile, yttrotitanite, wöhlerite, &c., for germanium. J. W. L.

Atomic Weight of Gold. By G. Krüss (*Ber.*, **21**, 126—130).—A controversial paper in reply to Thorpe and Laurie (Trans., 1887, 565, 866).

Mineralogical Chemistry.

An English Coal. By Scheurer-Kestner and Meunier-Dolfus (*Compt. rend.*, **105**, 1251—1255).—The coal was obtained from Glamorganshire. It gave 88 per cent. of coke and 3 to 4 per cent. of ash, the composition being as follows:—C 90·27, H 4·39, S 0·69, N 0·49, O 4·16. The composition of the volatile portion was C 22·53, H 34·96, O + N + S 42·51. The heat of combustion as actually determined (8864 cal.) differs considerably from that calculated by means of any of the usual formulæ. C. H. B.

Artificial Pyrochroite. By A. de Schulten (*Compt. rend.*, **105**, 1265—1267).—300 grams of pure potassium hydroxide was dissolved in 500 c.c. of water, boiled for some time in a flask through which a current of hydrogen or coal gas was passing, and a recently boiled solution of 15 to 17 grams of crystallised manganous chloride in 15 c.c. of water was introduced by means of a funnel with a stopcock. The flask was then heated to about 160°, when the whole of the manganous hydroxide dissolved. As the liquid cools, it deposits crystallised manganous hydroxide, and becomes almost solid. The crystals are washed with recently boiled water, alcohol, and ether, and dried at a gentle heat in a current of hydrogen. If sodium hydroxide is used, the precipitate does not dissolve even in concentrated solutions at 200°, but it becomes crystalline. Crystallised manganous hydroxide dissolves readily in hydrochloric acid and in a solution of ammonium chloride. When heated to redness in the air, it forms manganoso-manganic oxide, which retains the form of the original crystals. When heated in hydrogen, it yields manganous oxide, which is green when hot and grey when cold.

Manganous hydroxide under these conditions crystallises in flattened, transparent, regular, hexagonal prisms, with a reddish tint. The crystals are uniaxial, and the axis is negative, as in pyrochroite. Crystallised cadmium hydroxide likewise has a negative axis, but magnesium hydroxide, natural or artificial, has a positive axis. When the manganous hydroxide is pure, it alters very slowly in presence of air, but if it contains even a small quantity of alkali, it oxidises very quickly. C. H. B.

Mineralogical Notes. By G. F. Kunz (*Amer. J. Sci.*, **34**, 477—480).—1. *Rhodochroisite from Colorado.*—Rhodochroisite, in rich, red, transparent rhombohedra, has been found in the John Reed Mine at Alicante, Lake Co., Colorado. This is the first locality that has yielded crystals of such size (12 mm. across) and transparency. The sp. gr. is 3·69, and the hardness 3·5. Analysis gave the following results:—

MnO.	FeO.	CaO.	MgO.	CO_2.	Total.
58·33	3·61	nil	trace	(38·06)	100·00

2. *Hollow Quartz Crystals from Arizona.*—These crystals are found about 3 miles south-west of the town of Pinal, Pinal Co., Arizona. They occur in sandstone, penetrated in many places by spherules of obsidian. The crystals are mere walls surrounding hollow spaces much larger than the area of the wall itself.

3. *Hydrophane from Colorado.*—A white, opaque variety of hydrophane in rounded lumps, 5 to 25 mm. in diameter, has recently been brought from Colorado. It is remarkable for its power of absorbing water. When water is allowed to slowly drop on it, it first becomes white and chalky, and then gradually perfectly transparent. It was found by weighing that this mineral absorbs more than an equal volume of water.

4. *A Remarkable Nugget of Silver.*—One of the most remarkable nuggets of silver known was found in limestone at the Greenwood Mines in the State of Michoacan, Mexico. It weighed 606½ oz., and in its original state weighed 12 lbs. more. It consists of almost pure silver, and is entirely worn except in cavities where the form of some of the crystals is still visible. B. H. B.

Bismuthosphærite from Willimantic and Portland, Connecticut. By H. L. Wells (*Amer. J. Sci.*, **34**, 271—274).—The author has examined two specimens of basic bismuth carbonate, the composition of which appears to be identical with that of Weisbach's bismuthosphærite. The composition of that mineral has been considered doubtful by A. H. Chester (Abstr., 1887, 783), because no water was included in the analysis. In the Connecticut specimens, the percentage of water did not exceed 0·94. Since a part of the water found was probably hygroscopic moisture, and since the determinations were made by weighing the water in a calcium chloride tube, a method apt to give slightly high results, these two specimens of bismuth carbonate must be regarded as anhydrous. The analyses agree closely with the formula Bi_2O_3,CO_2. The existence of bismuthosphærite must thus be considered as established. B. H. B.

Natural Borates and Borosilicates. By J. E. Whitfield (*Amer. J. Sci.*, **34**, 281—287).—The author has repeated the analyses of some natural borates, in order to correct errors due to defective analytical methods. The boric acid was determined by the method devised by F. A. Gooch (Abstr., 1887, 299).

Colemanite from Death Valley, California, gave on analysis the following results:—

H_2O.	B_2O_3.	CaO.	MgO.	Total.
21·87	50·70	27·31	0·10	99·98

These results correspond with the formula $2CaO,3B_2O_3,5H_2O$. The same formula was calculated by J. T. Evans (Abstr., 1885, 958), from his analysis, in which the boric acid was determined by difference.

Priceite from Curry Co., Oregon, gave the following composition:—

H_2O.	B_2O_3.	CaO.	Total.
19·42	48·44	32·15	100·01

Pandermite from Panderma, in the Black Sea, gave on analysis the following results:—

H_2O.	B_2O_3.	CaO.	Total.
19·40	48·63	32·16	100·19

It will thus be seen that priceite and pandermite are identical in composition. The difference is solely in the physical character of the minerals, priceite being soft and friable, and pandermite hard and compact (compare Abstr., 1885, 1117).

Ulexite from Rhode's Marsh, Esmeralda Co., Nevada, gave on analysis the following figures:—

SiO_2.	Cl.	B_2O_3.	SO_3.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
0·04	2·38	43·20	0·28	14·52	10·20	0·44	29·46	100·52

The analysis being corrected for impurities, the formula $NaCaB_5O_9 + 6H_2O$ is deduced.

Ludwigite from Moravitza, in the Banat, gave on analysis the following results:—

B_2O_3.	Fe_2O_3.	FeO.	MgO.	MnO.	H_2O.	Total.
12·04	37·93	15·78	30·57	0·16	3·62	100·10

Tschermak obtained 16·09 per cent. of boric acid, but gives no water.

Datolite from Bergen Hill, New Jersey, gave—

SiO_2.	FeO.	CaO.	B_2O_3.	H_2O.	Total.
35·74	0·31	35·14	22·60	6·14	99·93

The formula is thus $B_2O_3,H_2O,2CaO,2SiO_2$.

Danburite from Russell, St. Lawrence Co., New York, gave—

SiO_2.	B_2O_3.	CaO.	$Fe_2O_3 + Al_2O_3$.	Ign.	Total.
49·70	25·80	23·26	1·02	0·20	99·98

Axinite from Cornwall (I), and from Bourg d'Oisans, Dauphiné (II), gave on analysis the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MnO.	MgO.	B_2O_3.	H_2O.	Total.
I.	42·10	17·40	3·06	5·84	20·53	4·63	0·66	4·64	1·80	100·66
II.	41·53	17·90	3·90	4·02	21·66	3·79	0·74	4·62	2·16	100·32

The formula is $BR'''_3R''_4H_2(SiO_4)_5O$. B. H. B.

Pseudomorphs in the Lead Mines of the Puy de Dome. By F. GONNARD (*Compt. rend.*, **105**, 1267—1269).—The enveloping pseudomorphs or perimorphoses consist of thin coatings of one mineral on the crystals of another. In the lead mines of the Puy de Dome, enveloping pseudomorphs of pyromorphite on cerussite or galena are frequently observed. Sometimes the mineral inside has undergone alteration, owing to the fact that the envelope has not protected it from the air, &c. Not unfrequently, when the layer of pyromorphite is of appreciable thickness, it is distinctly crystalline, and the hexagonal prisms can readily be recognised. It is obvious that an envelope of this character is not a true pseudomorph.

Another mineral found in the form of enveloping pseudomorphs is siderite. One specimen showed the unusual form of hexagonal prisms surmounted by rhombohedrons. Calcite does not occur associated with it, and hence it cannot be regarded as a pseudomorph after that mineral. The nature of the original mineral was not determined. The form is, however, possible for any substance crystallising in the rhombic system, and hence this is a case of siderite occurring as a pseudomorph under a form in which it might crystallise itself.

Pseudomorphs of pyrites on calcite were also found, the envelope of pyrites being crystalline, and showing combinations of the cube with the pentagonal dodecahedron. C. H. B.

Crystalline Compounds prepared by Ebelmen. By E. MALLARD (*Compt. rend.*, **105**, 1260—1265).—*Artificial phenacite*, $SiO_2,2BeO$, obtained by fusing beryllia and silica with borax, forms small, regular, hexagonal prisms with very brilliant faces, the optical sign being positive.

Beryllium chromite, BeO,Cr_2O_3, prepared by fusing chromic oxide with beryllia and boric anhydride, is a deep green powder, which polarises strongly under the microscope, and consists of minute crystals of a form identical with that of the variety of cymophane known as alexandrite. It is therefore analogous to the corresponding aluminium compound, the artificial cymophane likewise obtained by Ebelmen.

Crystallised niobic anhydride forms small, rhombic prisms with two perpendicular cleavages, h' and g', the angle mm being 140° 50′, and the horizontal parameters 0·355 : 1. The form seems to be pseudo-cubic; the acute positive bisectrix is perpendicular to h', the plane of the axes being p.

Tantalic anhydride was obtained in rhombic prisms with the faces g' h' well developed, and the subordinate faces m, g^2, g^3, g^5, the angle mm being about 143°. It follows that niobic and tantalic anhydrides are isomorphous.

Crystallised beryllia has the parameters $a : h = 1 : 1·6305$, the optical sign being positive. In crystallised zinc oxide, the parameters are $a : h = 1 : 1·6034$, and the optical sign is likewise positive. It follows that these two oxides are isomorphous, notwithstanding the difference in their specific volumes.

Aluminium borate, $B_2O_3,3Al_2O_3$, which Ebelmen analysed but did not describe, crystallises in rhombic needles, the dominant face being m truncated by g' and h'; angle mm = 91° 21′; acute positive bisectrix parallel with the vertical, the plane of the axes being parallel with g'.

The compound $3B_2O_3,2Fe_2O_3,9MgO$, which Ebelmen analysed, forms black, opaque prisms, which have very brilliant faces, and probably belong to the rhombic system. The principal faces are m and h', the angle mm being 90° 32′. An analogous compound containing chromium in place of iron forms a dark brown powder consisting of small prisms, which when examined by polarised light seem to belong to the rhombic system.

Ebelmen prepared crystallised tribasic borates, $B_2O_3,3RO$, which on his assumption that boric acid is analogous to silicic acid, are analogous to peridote, the oxygen ratio being 1 : 1; and likewise crystallised sesquibasic borates, which on the same assumption are analogous to enstatite. The tribasic borates actually obtained were the magnesium, manganese, and cobalt compounds. They are isomorphous, and belong to the rhombic system, the parameters being as follows:—

$B_2O_3,3MgO$	0·6412 : 1 : 0·5494	mm = 114° 40′
$B_2O_3,3CoO$	0·6461 : 1 : ?	mm = 114 15
$B_2O_3,3MnO$	0·6511 : 1 : 0·5351	mm = 113 52

The faces m are faces of cleavage, and the acute positive bisectrix is parallel with the vertical, the plane of the axes being g'. The principal indices of refraction for D are respectively 1·6748, 1·6537, 1·6527.

The sesquibasic borates obtained are the magnesium, manganese, and zinc compounds. They are isomorphous, and belong to the triclinic system, the parameters of the manganese compound being 1·8373 : 1 : 2·012, and *xy* = 76° 26′, *xz* 123° 58′, *yz* 92° 6′, *g′h′* 75·01, *ph′* 124° 29′, *pg′* 83° 16′. All have easy nacreous cleavage along *p*, and a less easy vitreous cleavage along *t*. The nacreous cleavage is almost always perpendicular to an optical axis. C. H. B.

Triclinic Felspars with Twinning Striations on the Brachypinacoid. By S. L. Penfield and F. L. Sperry (*Amer. J. Sci.*, **34**, 390—393).—The authors give the results of a careful study, in connection with the chemical composition of the felspars, of the striations due to twinning on $\infty\breve{P}\infty$ exhibited by very many cleavage specimens of plagioclase felspar, in addition to the ordinary striations on the basal plane. These striations on $\infty\breve{P}\infty$ have been shown by G. v. Rath (Abstr., 1878, 713) to have resulted from twinning according to the pericline law. The two individuals are united by a plane deviating slightly from the basal plane, passing through the macro-axis, and so inclined that the four plane angles it makes with the prisms $\infty'P$ and $\infty P'$ and the pinacoid $\infty\breve{P}\infty$ are all equal. This is the so-called rhombic section. Owing to the variations in the axial angles of anorthite felspars, the direction of the rhombic section changes considerably. The direction above the line parallel to the edge $0P : \infty\breve{P}\infty$ being regarded as positive, and that below as negative, the direction of the rhombic section in felspars of the albite-anorthite group was found by Tschermak to be as follows:—

			Na_2O per cent.	CaO per cent.
Albite, $Na_2Al_2Si_6O_{16}$ ..	Ab	+22°	11·8	0·0
Oligoclase...........	Ab_3An_1	+ 4	8·7	5·2
Andesine	Ab_1An_1	− 2	5·7	10·4
Labradorite	Ab_1An_3	− 9	2·8	15·3
Anorthite, $Ca_2Al_4Si_4O_{16}$	An	−18	0·0	20·1

	1.	2.	3.	4.	5.	6.
SiO_2	66·58	66·83	66·06	66·34	65·73	63·76
Al_2O_3	21·26	20·88	21·57	20·72	21·32	22·67
Fe_2O_3	0·07	0·25	0·18	—	0·12	0·41
CaO	1·18	1·46	1·80	1·85	1·95	3·05
Na_2O	10·26	10·36	9·57	9·44	9·66	6·89
K_2O	0·76	0·70	1·01	0·98	0·95	3·60
Ignition	0·16	0·27	—	0·38	0·19	0·40
Total	100·27	100·75	100·19	99·71	99·92	100·78
Sp. gr...............	2·610	2·632	2·633	2·627	2·628	2·622
Ratio An : Ab	1 : 16·0	1 : 13·0	1 : 9·6	1 : 9·2	1 : 9·0	1 : 4·1
Anorthite per cent. ..	5·87	7·25	8·94	9·20	9·70	15·17
Rhombic section	+12°	14°	13°	12°	10°	10°
Extinction on $\infty\breve{P}\infty$..	15	15	16	12	15	6°

In order to show the relation between the direction of the striations and the chemical composition of the felspars, the authors made analyses of cleavage specimens from six different localities, namely: 1, Branchville, Connecticut; 2, Hitterö, Norway; 3, Haddam, Connecticut; 4, Mineral Hill, Pennsylvania; 5, Danbury, Connecticut; 6, Pierrepont, New York. All the specimens show distinct striations on $\infty\breve{P}\infty$, and all satisfy Tschermak's formula as mixtures of $Na_2Al_2Si_6O_{16}$ and $Ca_4Al_4Si_4O_{16}$. The analytical results are given on the preceding page.

Judging from the above, it will be safe to predict that where the striations on $\infty\breve{P}\infty$ make an angle of about $+12°$, the felspar will be a mixture of albite with 5 to 10 per cent. of anorthite.

The authors have been unable to find many specimens of felspars more basic than oligoclase exhibiting striation on $\infty\breve{P}\infty$. The analysis of a specimen of labradorite from Labrador gave results in very satisfactory accord, both as regards the direction of the rhombic section and the extinction angle on $\infty\breve{P}\infty$, with the table given by Tschermak. Although the variation in the angles of plagioclase crystals is considerable, the change in position of the rhombic section from $+22°$ to $-18°$ is so great that the direction of the striations will clearly indicate what position any plagioclase holds in the albite-anorthite series.

B. H. B.

So-called Indicolite from Harlem. By R. B. Riggs (*Amer. J. Sci.*, **34**, 406).—A peculiarly bright blue mineral found at Harlem, New York, was supposed to be the rare variety of tourmaline known as indicolite. An analysis made by the author showed relations very different from those in tourmaline, the analytical results being as follows:—

SiO_2.	B_2O_3.	Al_2O_3.	MgO.	Na_2O.	K_2O.	Ignition.	Total.
34·82	4·07	55·30	0·57	1·76	1·04	2·96	100·52

The molecular ratios, deduced from the analysis, are closely expressed by the formula $3H_2O,(Na,K)_2O,10Al_2O_3,10SiO_2,B_2O_3$, a new borosilicate. A microscopic study of this blue mineral shows that the angle of extinction is very small. The mineral is undoubtedly biaxial with remarkable pleochroism (ultramarine, reddish-violet, colourless). Its structure is subfibrous, so as to render the angle of prismatic cleavage somewhat obscure. It is thus certain that the blue mineral is not indicolite, but in all probability a new borosilicate.

B. H. B.

Remarkable Crystals of Pyroxene from New York. By G. H. Williams (*Amer. J. Sci.*, **34**, 275—276).—Some yellowish-grey crystals of pyroxene occurring in the crystalline limestone of Orange Co., New York, have a peculiar tabular habit produced by the unusual development of the basal pinacoid. A remarkably fine group of these crystals, in the collection of the Johns Hopkins University, exhibits great singularity of form. It consists of six simple tabular crystals, and of two larger ones, which are at the same time twins and hemimorphic. The largest of these crystals measures 3 by 3½ cm. The upper portion shows the usual forms: $0P$, $-P$, P, $2P$, ∞P, $\infty\not{P}\infty$,

$\infty\bar{P}\infty$. Below, however, towards the front, there are only the forms 2P and $\bar{P}\infty$, indicating that the crystal is hemimorphic in the direction of the vertical axis. The lower back quarter of the crystal is exactly like the lower front quarter, but in a reversed position, so that the lower half of the crystal is a twin. The second crystal is essentially the same as the one just described. B. H. B.

Blue Clay from Farmington, Maine. By F. C. ROBINSON (*Amer. J. Sci.*, **34**, 407—408).—An analysis of blue clay from Farmington, Maine, gave the following results:—

SiO_2.	Al_2O_3.	FeO.	CaO.	Na_2O.	H_2O.	Total.
63·69	17·02	10·18	0·97	4·02	4·05	99·93

An approximate mechanical analysis gave the following percentages:—

Coarse sand.	Fine sand.	Fine clay.	Water.
3·73	22·97	69·25	4·05

The sand consisted principally of felspar, with traces of quartz and mica. The clay is used for brickmaking. B. H. B.

Meteorite from St. Croix Co., Wisconsin. By D. FISHER (*Amer. J. Sci.*, **34**, 381—383).—The mass of meteoric iron described was ploughed up in 1884 on a farm in Hammond Township. It weighed 53 lbs., and measured 8 by 8 inches across the face, with an average thickness of 5 inches. The character of the meteorite renders it probable that its fall did not precede the date of its discovery by many months. An analysis of the meteorite gave the following results:—

Fe.	Ni.	Co.	P.	SiO_2.	Total.	Sp. gr.
89·78	7·65	1·32	0·51	0·56	99·82	7·60—7·70

with traces of carbon, copper, and tin. Troilite is present in nodules 5 to 10 mm. in size. On the application of dilute nitric acid, the Widmanstätten figures quickly appear. These are cubical in arrangement. The meteorite now forms part of the Yale University collection at New Haven. B. H. B.

The Rockwood Meteorite. By J. E. WHITFIELD (*Amer. J. Sci.*, **34**, 387—390).—This meteorite was found in March, 1887, in a field 8½ miles west of Rockwood, Tennessee. Three pieces were found. The smallest measured 4 by 3 by 2¼ inches, and weighed 3 lbs. 10½ oz.; the next measured 7⅞ by 6½ by 2⅝ inches, and weighed 5 lbs. 13½ oz.; and the largest measured 14¾ by 10 by 8½ inches, and weighed 85 lbs. The mass is very brittle. Cut slices show irregularly shaped stony fragments, with metallic grains distributed through the mass. An analysis of the metallic portion gave 87·59 per cent. of iron, 12·09 per cent. of nickel, with traces of cobalt and copper, but neither phosphorus nor sulphur. An analysis of the stony portion gave the following results:—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	Fe.	Ni.	Cl.	P.	S.	Total.
41·92	9·27	22·94	9·09	8·76	3·75	1·74	0·18	0·65	1·58	99·88

This meteorite appears to be a lithosiderite poor in metal, the metallic portion not exceeding 16 per cent. of the mass. The stony part is probably anorthite and enstatite. B. H. B.

The Powder Mill Creek Meteorite. By G. F. KUNZ (*Amer. J. Sci.*, **34**, 476—477).—This meteorite is identical with the Rockwood meteorite (see preceding Abstract), and has been called from the Powder Mill Creek, because it fell in Cumberland Co.; Roane Co. in which Rockwood is situated being adjacent to this. The author is the possessor of a piece weighing 2000 grams. It resembles very closely the Hainholz, Westphalia, and the Taney Co., Missouri, meteorites. Its sp. gr. is 4·745. Chloride of iron (lawrencite) is present in considerable quantities. Under the microscope, clear crystals of anorthite and olivine were seen in the ground-mass of metallic iron. B. H. B.

Some American Meteorites. By G. F. KUNZ (*Amer. J. Sci.*, **34**, 467—477).—1. *The Taney Co., Missouri, Meteorite.*—This is supposed to have fallen in 1857 at a spot near Miney in Taney Co., 11 miles south-east of Forsyth. It was taken 60 miles to a farm in Limestone Valley, Arkansas, on the supposition that it was of value. In June, 1887, it came into the author's possession. It measures 34 by 35 by 29 cm. Its weight is 89·796 kilos. It is similar to the Hainholz, Westphalia, iron, and belongs to the logronite group of Meunier and the syssidères of Daubrée. Two large crystals of olivine are present, and at one corner of the mass there is a large inclosure of augite. The surface of the meteorite is deeply pitted, and exhibits traces of a black crust. An analysis of the metallic portion gave—

Fe.	Ni.	Co.	P.	Total.
89·41	10·41	0·29	0·16	100·27

The analysis of the stony portion gave—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	NiS.	FeS.	Total.
45·88	7·89	19·73	6·02	17·96	1·67	0·54	99·69

Further analyses of the finely ground stony portion show that the insoluble portion is enstatite only, and that the soluble portion is a lime-iron silicate containing 17 per cent. of alumina. The fragments described by C. U. Shepard (*Amer. J. Sci.*, **30**, 1860, 205) as the Forsyth iron, and by J. L. Smith (*ibid.*, **40**, 1865, 213) as the Newton Co., Arkansas, meteorite, are undoubtedly parts of the same meteorite which originally fell near Miney, in Taney Co.

2. *The Chattooga Co., Georgia, Meteorite.*—This mass was found on March 27th, 1887. In all, 12·5 kilos. were found. It is one of the

caillite group of Meunier, and has a sp. gr. of 7·615. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Total.
94·60	4·97	0·21	0·21	99·99

This iron does not bear the slighest resemblance to either of the Whitfield Co., Georgia, irons, found in the vicinity. It is a white iron, whilst the Walker Co., Alabama, iron has a bluish tinge and was found 100 miles due east.

3. *Meteoric Iron from Waldron Ridge, Claiborne Co., Tennessee.*—This was found in March, 1887, and supposed to be iron ore. The meteorite is one of the caillite group of Meunier. On the largest piece, weighing 15 lbs., the octahedral structure is very marked. The smaller pieces, weighing collectively several pounds, show considerable weathering. The iron separates readily at the cleavage plates, between which are thin leaves of schreibersite. Troilite and graphite were also observed. It thus appears that this meteorite is identical with the Cosby Creek, Cocke Co., the Sevier Co., the Greenbrier Co., and the Jennies Creek meteorites, which, although independently described, have been shown by Huntington to be parts of one meteorite. B. H. B.

Phosphatic Mineral Water. By BOURGOIN and CHASTAING (*J. Pharm.* [5], **16**, 337—341).—At Viry (Seine-et-Oise) is a spring found in a gallery cut in clay. The temperature of the water is constant at 4° even in summer, the yield is about 14 litres per minute, and though quite limpid at first a deposit is quickly formed.

A litre of water was found to contain—

Carbonic anhydride	0·17096 or 86·49 c.c.
Tricalcium phosphate	0·17901
Calcium hydrogen carbonate	0·21740
Magnesium hydrogen carbonate	0·03640
Calcium nitrate	0·04100
„ sulphate	0·05364
Sodium chloride	0·04130
Potassium chloride	traces
Lithium	sensible quantity
Silica	0·01980
Organic matter	0·00200
	0·76151

In an open flask, beautiful, lamellar crystals form after some days, which seem to be composed of calcium phosphate, and the water, originally acid, becomes sensibly neutral. J. T.

Composition of Certain Colliery Waters. By P. P. BEDSON (*J. Soc. Chem. Ind.*, **6**, 712—715).—The author gives the results, expressed in grams per litre, of the analyses of two colliery waters:—

	$FeSO_4$.	$BaCl_2$.	$CaCl_2$.	$MgCl_2$.	LiCl.	NaCl.	$CaSO_4$.
I.	—	1·372	21·058	3·127	0·358	59·265	—
II.	1·080	—	20·021	2·770	53·530		0·620

	$CaCO_3$.	$MgCO_3$.	Total.
I.	—	—	85·180
II.	0·134	0·021	78·176

I. Water from the Redheugh Colliery. This water drains from the Brockwell seam and adjacent rock. Temperature 13°. II. Water from the Wardley Colliery. This water is remarkable not only from its mineral constituents but also from the fact that it contains a large amount of gas dissolved in it.

The analysis of the gas showed it to have the following composition:—

CO_2.	CH_4.	N.
81·14	5·20	13·29

D. B.

Organic Chemistry.

Constitution of Nitroethane. By G. Götting (*Annalen*, **243**, 104—131).—By the action of ethyl iodide on nitroethane and sodium ethoxide in sealed tubes at 100°, a liquid of the composition C_5H_7NO is produced. It boils at 166—170° and is freely soluble in alcohol and ether. At a higher temperature, it decomposes, yielding pyridine and a resinous residue. Sodium iodide, sodium nitrite, and ammonium iodide, are formed as bye-products when ethyl iodide acts on sodium nitroethane. The nitrite and ammonium iodide are probably formed by secondary reactions. The primary reaction may be represented by the equation $9C_2H_5NO_2 + 6EtI + 6C_2H_5{\cdot}ONa = 6C_5H_7NO + 6C_2H_5{\cdot}OH + 9H_2O + 6NaI + 3NH_2{\cdot}OH$.

By substituting methyl, propyl and isobutyl iodides for ethyl iodide in the preceding experiment a series of homologous compounds is obtained having the composition—

	Boiling points.
C_4H_5NO	150—160°
C_5H_7NO	166—170
C_6H_9NO	175—178
$C_7H_{11}NO$	182—185

Each of the compounds is decomposed by distillation, yielding a volatile base. The formation of C_5H_7NO and its homologues can be more readily explained by Geuther's assumption that nitroethane is in reality acetamidoxide, $CH_3{\cdot}CO{\cdot}NH_2O$, than by V. Meyer's formula $CH_3{\cdot}CH_2{\cdot}NO_2$.

W. C. W.

Preparation of Hydrosulphides and Sulphides of Methyl and Ethyl. By P. KLASON (*Ber.*, **20**, 3407—3413).—Methyl hydrogen sulphide is prepared by diluting with ice a cold mixture of 750 c.c. of sulphuric acid and 500 c.c. of absolute methyl alcohol, and adding the whole to a solution of 2·75 kilos. of crystallised sodium carbonate. The solution is concentrated to such an extent that most of the sodium sulphate separates. The mother-liquor is then concentrated, mixed with a solution of 500 grams of potash in 1 litre of water, previously saturated with hydrogen sulphide, and heated on a water-bath. The gases evolved are passed first through a strong aqueous solution of 50 grams of potash, and then into a solution of 350 grams of potash in 700 c.c. of water. The small amount of hydrogen sulphide contained in the latter solution is precipitated with lead acetate, and the ethyl hydrogen sulphide liberated by the addition of hydrochloric acid. It is dried with potash and distilled. 500 c.c. of alcohol yielded about 200 grams of methyl hydrogen sulphide, and 40 grams of methyl sulphide. It is a thin, colourless, refractive liquid, having a very repulsive odour; it boils at 5·8° under 752 mm. pressure, and yields a crystalline hydrate with water (compare Gregory, *Annalen*, **15**, 239; and Obermeyer, this vol., p. 124).

Mercury methyl mercaptide, $Hg(SMe)_2$, is best prepared by passing methyl hydrogen sulphide through an aqueous solution of mercury cyanide; it is almost insoluble, and melts at 175°. The *lead compound*, $Pb(SMe)_2$, forms microscopic, crystalline plates; it is decomposed by exposure to air or light. The *bismuth compound*, $Bi(SMe)_3$, crystallises in yellow, microscopic needles; the *silver compound* forms a yellow, crystalline precipitate.

Ethyl hydrogen sulphide is prepared similarly to the methyl compound, using 1 litre of absolute alcohol, 500 c.c. of sulphuric acid, 4 kilos. of sodium carbonate, and 800 grams of potash. *Copper ethyl mercaptide*, CuSEt, not $Cu(SEt)_2$, is readily obtained when the mixed solutions of copper sulphate and sodium acetate are treated with ethyl hydrogen sulphide, and forms a pale yellow, amorphous powder. It was previously stated (*J. pr. Chem.* [2], **15**) that zinc and cadmium mercaptides are not decomposed by hydrochloric acid; later experiments show that all mercaptides with a positive metal are decomposed by hydrochloric acid.

Methyl sulphide is prepared by distilling a concentrated solution of methyl sodium sulphate (from $\frac{1}{2}$ litre of absolute methyl alcohol) with an aqueous solution of 500 grams of potash, previously half saturated with hydrogen sulphide. The yield is 150 grams. It boils at 37·2° under 758 mm. pressure. Ethyl sulphide may be prepared in a similar manner, and boils at 91·9°. Methyl ethyl sulphide is prepared by distilling a solution of methyl hydrogen sulphide (from 250 c.c. of alcohol) in potash with sodium ethyl sulphate (from 550 c.c. of alcohol); it boils at 66·9°. The yield was 160 grams.

N. H. M.

Alkyl Polysulphides. By P. KLASON (*Ber.*, **20**, 3413—3415).—When methyl hydrogen sulphide is passed into 100 grams of sulphur chloride, (S_2Cl_2), a product is obtained free from chlorine, probably consisting of methyl tetrasulphide, methyl trisulphide, and sulphur.

When distilled in a vacuum, methyl trisulphide passes over, and sulphur remains. Methyl trisulphide (Cahours, *Annalen*, **61**, 92) is a pale-yellow oil of a very disagreeable odour, boiling at 170° with slight decomposition. In a vacuum, it distils at 62°. Sp. gr. = 1·2162 at 0°; 1·2059 at 10°; and 1·119 at 17° (compared with water at 0°).

Paratolyl hydrogen sulphide reacts with sulphur chloride, yielding Otto's paratolyl tetrasulphide (Abstr., 1887, 954). N. H. M.

Sulphines and the Valency of Sulphur. By H. KLINGER and A. MAASEN (*Annalen*, **243**, 193—218).—The authors have repeated Krüger's experiments (this Journal, 1877, i, 186) on isomeric sulphine compounds, and they prove that the diethylmethylsulphine iodide, prepared by the action of methyl iodide on diethyl sulphide, is identical with the product of the action of ethyl iodide on methyl ethyl sulphide. This is shown by an examination of the platino-, auro-, and mercuro-chlorides, and also of the cadmio-iodide.

Dimethylethylsulphine iodide, SMe_2EtI, is formed not only by the action of methyl iodide on ethyl methyl sulphide, but also by the action of methyl sulphide on ethyl iodide. It is a hygroscopic, crystalline substance, soluble in alcohol, and is precipitated from the alcoholic solution by ether. It melts at 108—110°. The *cadmio-iodides*, $2SMe_2EtI,CdI_2$, melting with slight decomposition at 179°, and SMe_2EtI,CdI_2, melting at 98—99°, were prepared. The *mercurochlorides*, $SMe_2EtCl,2HgCl_2$ and $SMeEt_2Cl,6HgCl_2$, melt at 118° and 200° respectively. The *platinochloride*, $2C_4H_{11}SCl,PtCl_4$, forms orange-red crystals belonging to the regular system. It is insoluble in alcohol and ether. The *aurochloride*, $C_4H_{11}SCl,AuCl_3$, forms minute crystals melting at 240—244°.

As the supposed existence of Krüger's isomeric sulphines forms the sole argument in favour of the view that the four affinities of the sulphur-atom are of dissimilar nature, the author's results show that there is no longer any experimental evidence in support of this hypothesis. W. C. W.

Disulphones. By E. FROMM (*Ber.*, **21**, 185—188).—When bromethylidenediethylsulphone (Abstr., 1887, 123) is heated with aqueous potash, it is converted into ethylidenediethylsulphone; the yield, however, does not amount to that theoretically possible, and inasmuch as sulphuric acid is one of the products of the reaction, it is probable that hydroxyethylidene disulphone is formed, but acting as an oxidising agent is itself reduced to ethylidenedisulphone.

When ethylidenediethylsulphone, which melts at 75—78° and not at 60°, as stated by Escales and Baumann (*ibid.*), is dissolved in anhydrous ether or benzene, and treated with sodium, hydrogen is evolved and a compound obtained which could not be purified; diethylsulphonedimethylmethane (Baumann, *ibid.*) is, however, obtained if methyl iodide is added to the solution before treatment with sodium. A like reaction occurs when an alcoholic solution of the disulphone is boiled with methyl iodide and alcoholic potash. Diethylsulphonedimethylmethane when treated in benzene solution with sodium does not evolve hydrogen. W P. W.

Synthetical Experiments in the Sugar-group. By E. FISCHER and J. TAFEL (*Ber.*, **20**, 3384—3390; compare this vol., p. 39).—Glycerosazone (Abstr., 1887, 651) is prepared by adding 15 parts of bromine to a solution of 10 parts of glycerol and 35 parts of crystallised sodium carbonate in 60 parts of water at 10°. 200 grams of glycerol can be used in one operation. The solution is treated with 5 parts of phenylhydrazine hydrochloride. In five to eight days, the glycerosazone separates as a yellow, crystalline precipitate. The yield is 20 per cent. of the weight of glycerol.

When the oxidised glycerol is treated with aqueous soda, so that the amount of free alkali amounts to 1 per cent., and is kept for four to five days, the liquid loses the power of reducing alkaline copper solution in the cold; when warmed, it still has the power of reducing copper solutions. The solution is neutralised with acetic acid, and heated with phenylhydrazine hydrochloride and sodium acetate for six to eight hours. The product contains two osazones, $C_{18}H_{22}N_4O_4$. The one has all the properties previously ascribed to α-acrosazone (from acrylaldehyde bromide); it crystallises from alcohol in pure yellow, well-formed needles, which melt at 217° with decomposition. The other osazone is more readily soluble in ethyl acetate, from which it crystallises in globular groups of slender needles melting at 158—159°; it is probably identical with β-acrosazone. This method for preparing the acrosazones is more convenient than that previously described.

When a solution of 5 grams of dulcitol and 12 grams of sodium carbonate in 40 c.c. of water is treated with 5 grams of bromine, and the whole, half an hour afterwards, is warmed with 5 grams of phenylhydrazine and 5 grams of sodium acetate, the *osazone*, $C_{18}H_{22}N_4O_4$, separates in yellow flakes. This closely resembles galactosazone (Abstr., 1887, 562) except that it melts at 205—206° with decomposition. The name *phenyldulcitosazone* is ascribed to the new compound.

N. H. M.

Condensation of Formaldehyde. By O. LOEW (*Ber.*, **21**, 270—275).—The condensation of formaldehyde (Abstr., 1886, 609) is most readily effected by the action of strong bases, although it can be brought about by salts having an alkaline reaction, such as potassium sulphite or carbonate; salts having a neutral reaction are, however, without action on the aldehyde. Comparative experiments at 100° with aqueous solutions of lime and baryta containing equimolecular proportions of the two bases showed that the former rapidly acted on the aldehyde (15 per cent. solution) with the formation of formose as chief product, whilst the action of the latter resulted in the production of formic acid, much aldehyde remaining unaltered owing to the consequent neutralisation of the base. The production of formose by the action of lime-water is accelerated by the addition of sodium chloride, which itself does not bring about the condensation of the aldehyde, but is retarded by the presence of sodium acetate, potassium nitrate, and of much copper, iron, or tin. Calcined magnesia does not react with formaldehyde either in the cold or at 100°, but an aqueous solution of the hydroxide converts it into formose at 100°. Litharge and many lead salts also effect the condensation of the aldehyde, and metallic lead acts in like manner; it is probable, however, that in this case the action is due to the presence of traces of the oxide, since the amount of the latter dissolved by shaking litharge with distilled water for some hours, adding 0·1 per cent. of the aldehyde, filtering and heating at 100° for two hours, sufficed to form formose. Iron, tetrethylammonium hydroxide, and many organic bases, also bring about the condensation.

When the osazone (m. p. = 123°) obtained from the sugar formed by heating a 0·5 per cent. solution of formaldehyde with tin for 15 hours (*ibid.*, 864) is heated in alcoholic solution at 100° for 25 to 30 hours, the melting point is found to have risen to 148°, at which it remains constant. A sugar, *β-formose*, which directly yields an *osazone*, $C_{18}H_{22}N_4O_3$, crystallising in small, yellow needles melting at 148°, is formed when a 0·1 per cent. solution of formaldehyde is heated for five hours with much tin. It is a thick, sweet, non-fermentable syrup, does not become brown at 100°, yields humous substances with hydrochloric acid, and its solution in alcoholic hydrogen chloride yields a wine-red colour with resorcinol, and a steel-blue colour with diphenylamine. 100 c.c. of Fehling's solution are reduced by 0·073 gram of the sugar.

If formaldehyde is added to an aqueous solution of magnesium hydroxide, prepared by treating a 5 to 10 per cent. solution of magnesium sulphate with litharge, until the mixture contains 0·3 per cent. of the aldehyde, and the whole is digested at 100° for many hours, a mixture of at least two non-fermentable sugars is obtained, one of which yields an *osazone* crystallising from benzene in yellow needles melting at 152°. W. P. W.

Solubility of Calcium and Barium Formates, Acetates, and Propionates. By E. v. Krasnicki (*Monatsh.*, 8, 595—606).—The solubilities of the different salts were determined by Raupenstrauch's method. The formulæ deduced from these determinations are given below:—

Calcium formate, $S = 16{\cdot}2978 + 0{\cdot}03229(t - 0{\cdot}8) - 0{\cdot}0001254(t - 0{\cdot}8)^2$

Barium formate, $S = 27{\cdot}7744 + 0{\cdot}0236743(t - 1) + 0{\cdot}0063622(t - 1)^2 - 0{\cdot}000060122(t - 1)^3$

Calcium acetate, $S = 37{\cdot}8512 - 0{\cdot}2575(t - 1) + 0{\cdot}0058845(t - 1)^2 - 0{\cdot}0000475576(t - 1)^3$

Barium acetate, $S = 58{\cdot}473 + 0{\cdot}65067(t - 0{\cdot}8) - 0{\cdot}005431(t - 0{\cdot}8)^2$

Calcium propionate, $S = 41{\cdot}2986 - 0{\cdot}11196(t - 0{\cdot}2) + 0{\cdot}000085065(t - 0{\cdot}2)^2 + 0{\cdot}0000117907(t - 0{\cdot}2)^3$

Barium propionate, $S = 48{\cdot}2071 + 0{\cdot}371205(t - 0{\cdot}6) - 0{\cdot}0015587(t - 0{\cdot}6)^2$.

The solubilities of the isobutyrates, isovalerates, and methylethylacetates, have been given by Sedlitzky (this vol., p. 250).

A. J. G.

Temperature of Conversion of Copper Calcium Acetate. By L. T. Reicher (*Zeit. physikal. Chem.*, 1, 221—226).—That there is a temperature at which the crystals of this salt are converted into crystals of copper acetate and calcium acetate, is already rendered probable by the experiments of Kopp and Schuchardt. Microscopical examination confirms this supposition, for on heating the double salt up to about 80°, it separates into colourless needles of calcium acetate and green rhombic crystals of copper acetate. To determine the temperature of conversion exactly, a dilatometer was employed. The dilatometer was filled with the powdered double salt, exhausted and filled with mercury, and the change of volume at a given temperature was observed. It was found that the temperature of conversion lies between 78° and 76·2°. C. S.

Preparation of β-Iodopropionic Acid. By V. Meyer (*Ber.*, **21**, 24—25).—The author describes in detail various modifications of the method previously given for the preparation of β-iodopropionic acid (Abstr., 1887, 232). F. S. K.

Analogy between Ketonic Acids and the Alkyl Sulphones of the Fatty Acids. By R. Otto (*Ber.*, **21**, 89—99).—The larger portion of this paper deals with the points of analogy between the ketonic acids and the alkyl sulphones of the fatty acids.

β-Phenylsulphonepropionic acid, $SO_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is prepared by neutralising β-iodopropionic acid and benzenesulphinic acid with sodium carbonate, and heating the product until no more water is given off. It forms shining, monosymmetrical or asymmetrical plates, is sparingly soluble in cold water, somewhat more soluble in ether, and melts at 123—124°. The alkali salts are described. The ethyl salt is a thick oil of a yellow colour, readily soluble in alcohol and ether, insoluble in water. The free acid is very stable; it does not react with the halogens, is not attacked by potash at 180°, but is totally decomposed at 280°; it is speedily reduced by sodium amalgam, the group $PhSO_2$ yielding a sulphinate. J. W. L.

Isodibromosuccinic Acid. By R. Demuth and V. Meyer (*Ber.*, **21**, 264—270).—A repetition of Beilstein and Wiegand's experiments on isodibromosuccinic acid (Abstr., 1882, 1051) shows that bromofumaric acid and not pyruvic acid is formed with the evolution of some carbonic anhydride when the barium salt is treated with moist silver oxide in the dark. Bromofumaric acid is also formed when the acid is heated with water for 10 hours in a reflux apparatus (Kekulé, *Annalen*, Suppl. **2**, 90), and racemic acid is obtained when the silver salt of the acid is boiled with water. Hence the unsymmetrical formula $COOH{\cdot}CH_2{\cdot}CBr_2{\cdot}COOH$ can no longer be ascribed to this acid. Attempts to prepare an acid of this formula by the oxidation of *αα*-dibromobutyric acid, $EtCBr_2{\cdot}COOH$, by displacing the oxygen of the carbonyl-group in acetoxalic acid by bromine, and by treating ethyl sodiomalonate with ethyl tribromacetate and saponifying the product led to no result, the crystalline compound formed in the last experiment being free from bromine, whilst ethyl tricarbintetracarboxylate, when treated with 1 mol. of bromine at 140° (compare Abstr., 1883, 46), yields a compound which on hydrolysis with concentrated hydrobromic acid yields carbonic anhydride and a crystalline compound free from bromine, and not symmetrical dibromosuccinic acid. W. P. W.

Ethyl Oxalacetate. By W. Wislicenus (*Ber.*, **20**, 3392—3394; compare Abstr., 1887, 234).—Ethyl oxalacetate is prepared by shaking a solution of ethyl oxalate in four parts of ether with sodium ethoxide, previously freed from alcohol by heating in a current of hydrogen at 200°. The product is treated with ethyl acetate when the sodium compound separates; the yield is 70 per cent. of the theoretical. Ethyl oxalacetate boils at 131—132° under 24 mm. pressure, and reacts with ammonia and with aniline, yielding crystalline compounds. The *phenylhydrazine-derivative*, $C_{14}H_{18}N_2O_4$, crystallises in plates melting at 76—78°. When an alcoholic solution of the ethyl salt is treated with carbamide, the compound $C_9H_{14}N_2O_5 + EtOH$ separates in colourless crystals. The *hydroxylamine-derivative* is an oil. Nitrous acid reacts with ethyl oxalacetate in the cold, with formation of a crystalline isonitroso-derivative. N. H. M.

Ethyl Methyloxalacetate. By W. Wislicenus and E. Arnold (*Ber.*, **20**, 3394—3396).—*Ethyl methyloxalacetate*, $C_9H_{13}O_5Na$, is prepared by the action of sodium ethoxide and ethyl propionate on ethyl oxalate dissolved in ether. It forms a colourless oil, boiling at 137—138° under 23 mm. pressure, insoluble in water, readily soluble in alcohol, ether, and alkali; the alcoholic solution gives an intense red coloration with ferric chloride. When boiled with alcoholic potash, it is converted into oxalic and propionic acids. Boiling dilute sulphuric acid decomposes it with formation of propionylformic acid (Claisen and Moritz, Trans., 1880, 691). The *phenylhydrazine-derivative* of propionylformic acid, $CH_2Me\cdot C(N_2HPh)\cdot COOH$, crystallises from dilute alcohol in plates melting at 144—145°; when warmed with sulphuric acid and alcohol, and precipitated with water, *scatolecarboxylic acid*, $C_6H_4<\substack{CMe\\NH}>C\cdot COOH$, is obtained; this melts at 164—165°, decomposing into scatole and carbonic anhydride, and differs from Salkowski's compound (Abstr., 1885, 568) in its crystalline form and in being more sparingly soluble.

N. H. M.

Cryoscopic Studies on Racemic Acids and Racemates. By F. M. Raoult (*Zeit. physikal. Chem.* **1**, 186—189).—In the case of solutions containing not more than 5 per cent. of acid, observation shows that equal quantities of dextrotartaric acid and racemic acid produce the same lowering of the freezing point, and it is inferred that the racemic acid is completely decomposed. For solutions of greater concentration, this will not be the case; part only will be decomposed. The fall of temperature produced by each unit of mass of this part will be known by observation. For the other, the fall caused by each unit may be calculated from the law that the molecular fall of the freezing point is equal to 19 for all organic acids. The actual fall of temperature caused by the whole amount of racemic acid can be observed, and a simple equation will then give the amount of racemic acid decomposed. Thus it was found that out of 14·229 grams of racemic acid dissolved in 100 grams of water, 0·880 gram remained undecomposed.

In the case of the compounds, $C_4H_4O_6(NH_4)Na + 4H_2O$ and $2[C_4H_4O_6(NH_4)Na + H_2O]$, the fall of temperature is the same for solutions of the same strength up to about 13 per cent. C. S.

Organic Fluorine Compounds. By O. Wallach and F. Heusler (*Annalen*, **243**, 219—244).—In the preparation of fluorbenzene (Abstr., 1887, 130), phenol and diphenyl ether, Ph_2O, are obtained as bye-products. Fluorbenzene can be obtained as a crystalline mass by exposure to the temperature produced by ether and solid carbonic anhydride. The index of refraction for Frauenhofer's line C is 1·4635; $\Delta_0 = 0·00017$. *Parafluoronitrobenzene* melts at 26·5°. *Parafluoraniline* can be solidified by means of solid carbonic anhydride. The *acetyl*-derivative, $C_6H_4F{\cdot}NHAc$, melts at 150—151°. *Fluorbenzeneparadiazopiperidide*, $C_6H_4F{\cdot}N_2{\cdot}C_5H_{10}$, is an unstable crystalline substance. *Paradifluorobenzene*, $C_6H_4F_2$, is liquid at the ordinary temperature. Its sp. gr. is about 1·11, and it boils between 87° and 89°.

Parafluorochlorobenzene, C_6H_4FCl, prepared from parafluoraniline by means of Sandmeyer's method, boils at 130—131°. Its sp. gr. at 15° is 1·226. *Parafluorobromobenzene* melts between —15° and —20°, and boils at 152—153°. Sp. gr. 1·593 at 15°. *Parafluoriodobenzene* is prepared by the action of hydriodic acid on freshly prepared pure fluorbenzenediazopiperidide. It boils at 182—184°, and is decomposed by strong nitric acid, yielding iodine and fluornitrobenzene. *Parafluorphenol* boils at 186—188°.

Pseudocumenediazopiperidide, $C_6H_2Me_3{\cdot}N_2{\cdot}C_5NH_{10}$, is deposited from alcohol in thick prisms and melts at 50°. It is decomposed by hydrofluoric acid, yielding *fluoropseudocumene*, $C_6H_2Me_3F$, which melts at 27° and boils at 174—175°. Chloropseudocumene melts at 70—71° and boils at 213—215°. The bromo-derivative melts at 72° and boils at 233—235°. *Iodopseudocumene* melts at 37° and boils at 256—258°. Pseudocumenol melts at 71° and boils at 234—235°. *Difluorodiphenyl*, $C_{12}H_8F_2$, is crystalline, and dissolves freely in alcohol and ether. It melts at 88—89° and boils at 254—255°. Although Sandmeyer's method of converting amido-compounds into chloro- and bromo-substitution products yields admirable results, it is not to be recommended in the case of fluorides; the decomposition of diazoamido-compounds by hydrofluoric acid almost invariably yields better results in the latter case.

A comparison of the boiling points and specific gravity of the preceding compounds shows that (1) the substitution of hydrogen by fluorine increases the specific gravity, and has very slight influence on the boiling point; (2) the difference in boiling point between corresponding iodine and bromine substitution products, and between bromine- and chlorine-derivatives is much smaller than the difference between chlorine and fluorine substitution products. The authors conclude that the boiling point of liquid fluorine is much lower than that of chlorine, and that it is probably near the boiling point of hydrogen.

Numerous experiments show that fluorine unites more firmly with carbon than chlorine, bromine, or iodine do. W. C. W.

Dichroïns. By H. Brunner and P. Chuit (*Ber.*, **21**, 249—256).—Further experiments have confirmed the view put forward by Brunner and Krämer (Abstr., 1884, 1354) that compounds analogous to Liebermann's colouring matters (this Journal, 1874, 693) are formed only from paranitrosophenol and those polyhydric phenols in which two hydroxyl-groups are in the meta-position relatively to one another. These compounds are now termed *dichroïns* from their fluorescent and dichroïc properties, and are divided into two groups termed α- and β-dichroïns respectively. The α-dichroïns contain the group $C_6N(O{\cdot}C_6)_2$, and comprise the colouring matters, $C_{18}H_{15}NO_3$, derived from phenol (Abstr., 1884, 1341), $C_{18}H_{15}NO_6$ and $C_{36}H_{28}N_2O_{10}$ from resorcinol (Abstr., 1885, 525), and $C_{21}H_{21}NO_6$ from orcinol (*ibid.*); whilst the β-dichroïns contain the group $C_6{\cdot}N{<}\substack{O\\O}{>}C_6$, and comprise the colouring matter, $C_{14}H_{11}NO_3$, derived from orcinol (*ibid.*), together with azoresorcinol, azoresorufin (Abstr., 1884, 1333), and azoresorufyl ether, $C_{48}H_{50}N_4O_{13}$ (*Ber.*, **18**, 586), the last three compounds being termed β-resorcinol-, di-β-resorcinol-, and tetra-β-resorcinol-dichroïn respectively. In the majority of reactions by which dichroïns are formed, other colouring matters are also obtained differing from them in containing more oxygen and being destitute of fluorescence; these are termed oxychroïns.

Acetyl-α-phenoldichroïn, $OAc{\cdot}C_6H_4{\cdot}NO(OPh)_2$, prepared by heating α-phenoldichroïn (1 part) with acetic anhydride (3 parts) and anhydrous sodium acetate (2 parts) at 140° for an hour, is a brown, amorphous mass soluble in ether, alcohol, &c. *Acetylphenoloxychroïn*, $OAc{\cdot}C_6H_4{\cdot}N(OPh)_2$, was also prepared.

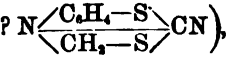
Orcinoldichroïn has the formula $C_6H_2(OH)_2Me{\cdot}N(O{\cdot}C_6H_2Me{\cdot}OH)_2$; its *acetyl*-derivative, $C_{21}H_{17}(OAc)_4NO_6$, is a brown, amorphous mass soluble in ether, alcohol, &c.

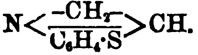
Thymoldichroïn was prepared by Liebermann's method (this Journal, 1875, 167), and when freed from unattacked thymol has the composition $O[N(C_6H_2MePr{\cdot}OH)_2]_2$. It sublimes at 140° with partial decomposition forming violet-coloured vapours, and is a dark-violet, amorphous mass, soluble in alcohol, ether, chloroform, and benzene yielding red solutions showing pale-green fluorescence. The *acetyl*-derivative, $C_{40}H_{48}(OAc)_4N_2O_5$, is a brown, amorphous mass, soluble in alcohol, ether, &c. In the purification of thymoldichroïn by steam distillation, thymoquinone passes over with the steam. Experiments show, however, that it is not a decomposition-product of thymoldichroïn, and to explain its formation the authors point out that nitrosothymol, unlike nitroso-phenol, -resorcinol, and -orcinol, seems to act as a quinoneoxime in the formation of its dichroïn, and regard it as probable that in addition to this reaction a second also occurs in which a portion of the thymol reacts with thymoquinoneoxime to form amidothymol and thymoquinone (compare Sutkowski, Abstr., 1887, 41).

W. P. W.

Formation of Secondary Aromatic Amines. By A. PICTET (*Ber.*, **20**, 3422—3424).—Ethylacetanilide is prepared by adding 75 grams of finely-powdered acetanilide to a cold solution of 31 grams of caustic potash in 300 grams of 95 per cent. alcohol; after a short time the flask containing the mixture is fitted with a reflux condenser, 65 grams of ethyl bromide is added, and the whole slightly warmed on a water-bath. When the reaction becomes less violent, the mixture is heated for one to two hours, allowed to become cool, and filtered. The advantages of this method over Hepp's (*Ber.*, **10**, 327) are that it does not involve the use of large amounts of sodium, and that the product is more easily purified. The yield of ethylaniline (41 per cent. of the theoretical) is, however, not so good as that obtained by Hepp's method. In the case of formanilide, the yield is almost theoretical.

N. H. M.

Action of Sulphur on Dimethylaniline and Methylaniline. By R. MÖHLAU and C. W. KROHN (*Ber.*, **21**, 59—67).—When dimethylaniline is boiled with sulphur for 12 hours and distilled, an oil boiling at 210—345° is obtained. When this is treated with hydrochloric acid, it is separated into an oil of indifferent character which soon solidifies, and a mixture of several basic compounds. From the latter, Hofmann's methenylamidophenyl mercaptan (Abstr., 1887, 823, 1039), aniline, and methylaniline were separated. The indifferent crystalline substance has the formula $C_8H_7NS_2$ (?  $N\langle{}^{C_6H_4-S}_{CH_2-S}\rangle CN$), melts at 88—89°, and boils above 360°. When boiled with sulphur, it is converted into methenylamidophenyl mercaptan, and seems therefore to be the primary product. When treated with nitric acid, the compound $C_8H_7NS_2$ is changed into the base C_8H_7NS, probably



$$N\langle{}^{-CH_2-}_{C_6H_4 \cdot S}\rangle CH.$$

By the action of sulphur on methylaniline, the same compounds are obtained. The authors think that at first a decomposition of 2 mols. of methylaniline into dimethylaniline and aniline must have taken place, the dimethylaniline so formed then reacting with sulphur as described above.

J. W. L.

Action of Thiocarbonyl Chloride on Secondary Amines. By O. BILLETER and A. STROHL (*Ber.*, **21**, 102—110).—*Propylphenylthiocarbamine chloride*, CSCl·NPhPr, crystallises from light petroleum in thick, colourless prisms melting at 36°. It is more stable in damp air than the corresponding methyl and ethyl compounds. *Dipropylthiocarbanilide*, $CS(NPhPr)_2$, forms colourless plates melting at 103·5°. *Methylpropylthiocarbanilide*, NPhMe·CS·NPhPr, prepared either from methyl chloride and propylaniline or from propyl chloride and methylaniline, forms colourless prisms melting at 56·5°.

Ethylpropylthiocarbanilide, NPhPr·CS·NPhEt, is prepared like the last-named compound and melts at 66·3°. All these derivatives dissolve easily in concentrated acetic, hydrochloric, and sulphuric acids without change, whereas by warming with concentrated sulphuric acid or heating at 150° with hydrochloric acid the secondary base is readily eliminated.

Alcohols and phenols, the corresponding sulphur compounds, and also their metallic salts, react readily with the thiocarbamine chlorides already described, with formation of the corresponding thio- and dithio-carbamic acids. Of this series, the following were prepared:—*Ethyl ethylphenylthiocarbamate*, NEtPh·CS·OEt, prepared by the action of ethyl phenylcarbamine chloride on sodium ethoxide in ethereal solution, distils at 143·6° under a pressure of 12 mm. Sp. gr. 1·066 at 15°. It solidifies by prolonged cooling to a colourless, crystalline mass which melts at 18°. *Phenyl ethylphenylthiocarbamate*, NEtPh·CS·OPh, forms colourless needles and melts at 69·2°. *Phenyl ethylphenyldithiocarbamate*, NPhEt·CSSPh, crystallises in compact, colourless needles, and melts at 127·8°. *Ethyl ethylphenyldithiocarbamate* melts at 66·4°. A trisubstituted thiocarbamide is formed by the action of ethyl phenylthiocarbamine chloride, aniline, &c., and can be isolated by stopping the reaction after the mass first solidifies. It is decomposed if the reaction proceeds too far into thiocarbanilide and aniline hydrochloride. A small quantity of a dithiobiuret is also formed. The dithiobiurets are readily obtained by the further action of thiocarbamine chloride on the tertiary carbamides first formed.

Dimethyltriphenyldithiobiuret, $C_2S_2N_3Ph_3Me_2$, prepared from methylphenylthiocarbamine chloride and methylthiocarbanilide, forms yellow needles melting at 202·5°. It is sparingly soluble in alcohol and ether, readily so in chloroform.

Diethyltriphenyldithiobiuret, $C_2S_2N_3Ph_3Et_2$, prepared from ethylphenylthiocarbamine chloride and ethylthiocarbanilide, crystallises in lemon-yellow needles melting at 158°. It is more readily soluble than the methyl compound.

Methylethyltriphenyldithiobiuret, (*a*), NEtPh·C(NPh)·S·CS·NMePh, prepared from methylphenylcarbamine chloride and ethylthiocarbanilide, forms small, pale yellow needles melting at 157·5°. It is soluble in chloroform, sparingly soluble in alcohol and ether. (*b*.) NMePh·C(NPh)·S·CS·NEtPh, prepared from ethylphenylcarbamine chloride and methylthiocarbanilide, forms small, light-yellow needles like those of the (*a*) compound, and melts at 156·5°.

Dipropyltriphenyldithiobiuret, $C_2S_2N_3Pr_2Ph_3$, prepared from propylphenylcarbamine chloride and propylthiocarbanilide, forms shining, yellow needles melting at 153·7°. It is soluble in chloroform.

Methylpropyltriphenyldithiobiuret, $C_2S_2N_3MePrPh$ (*a*), prepared from methylphenylcarbamine chloride and propylthiocarbanilide, crystallises in shining yellow pyramids, melting point 110°; (*b*) prepared from propylphenylcarbamine chloride and methylthiocarbanilide, forms yellow pyramids similar to the (*a*)-derivative, and melts at 111°.

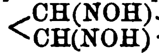
Ethylpropyltriphenyldithiobiuret, $C_2S_2N_3EtPrPh_3$, (*a*) prepared from ethylphenylthiocarbamine chloride and propylthiocarbanilide, crystallises in pale yellow needles melting at 165·8°. Very sparingly soluble in alcohol; (*b*) prepared from propylphenylthiocarbamine chloride and ethyl thiocarbanilide, crystallises in yellow needles melting at 165°.

Propylthiocarbanilide, $CSN_2H·Pr·Ph_2$, prepared from propylaniline and phenyl isothiocyanate, consists of colourless, shining needles which melt at 104·3°. It is readily soluble in alcohol, and is decomposed by hydrochloric acid into its components. J. W. L.

Constitution of Mixed Azo-compounds. By V. MEYER (*Ber.*, **21**, 11—18).—The author had independently arrived at views on the constitution of the mixed azo-compounds identical with those brought forward by Japp and Klingemann (Proc., 1887, 140).

Compounds of Phenylhydrazine with Ketone Alcohols. By H. LAUBMANN (*Annalen*, **243**, 244—248).—*Benzoylcarbinolphenylhydrazone*, $N_2HPh:CPh·CH_2·OH$, crystallises in needles, melts at 112°, and dissolves freely in alcohol and ether. It is converted into an amorphous product, probably hydroxyphenylindole, by the action of zinc chloride at 150°. The hydrazone is converted into the osazone, $N_2HPh:CPh·CH:N_2HPh$, by treatment with phenylhydrazine and sodium acetate in alcoholic solution. The osazone melts at 152° and is soluble in ether, benzene, and in hot alcohol.

The *osazone of acetol* is identical with the product v. Pechmann (Abstr., 1887, 1103) obtained by the action of phenylhydrazine on nitrosoacetone. W. C. W.

Action of Phenylhydrazine on Dioximes. By M. POLONOWSKY (*Ber.*, **21**, 182—184).—When glyoxime in alcoholic solution is treated with an equimolecular proportion of phenylhydrazine, an additive compound,  $<\begin{matrix}CH(NOH)\\CH(NOH)\end{matrix}>NH_2·NHPh$, is obtained. This crystallises from alcohol in white scales, melts at 110°, and is readily soluble in alcohol, less so in ether, and insoluble in water. Concentrated aqueous soda dissolves it, and the solution when heated yields phenylhydrazine; a like decomposition is also produced by concentrated sulphuric acid.

Under similar conditions diphenylglyoxime yields an additive compound, $C_{20}H_{20}N_4O_2$, which crystallises in needles, melts at 149—150°, and closely resembles the preceding derivative in its properties.

β-Naphthaquinonedioxime, in like manner, forms an additive compound, $C_{16}H_{16}N_4O_2$. This crystallises from alcohol in tufts of long needles, begins to fuse at 105°, and melts at 138°. W. P. W.

Aldines and Amidoacetophenone. By E. BRAUN and V. MEYER (*Ber.*, **21**, 19—21).—When isonitrosoacetophenone is reduced in hydrochloric acid solution, it is completely transformed into the hydrochloride of an amidoacetophenone, $COPh·CH_2·NH_2$. This salt crystallises from water in large, hard, colourless crystals, and is very stable; it can be recrystallised from hot water, and forms a crystalline platinochloride. The freshly precipitated base redissolves in acids, but when purified by washing or recrystallising from alcohol, it becomes orange-coloured, and completely loses its basic properties, being converted into a coloured crystalline substance, which resembles isoindole very closely, and with which it is probably identical. A ketine, $N\left\langle\begin{matrix}CPh : CPh\\ CPh : CPh\end{matrix}\right\rangle N$, is readily obtained from the monoxime of benzil. F. S. K.

Formation of Phenylhydrazile Acids from the Anhydrides of Bibasic Acids. By R. Anschütz (*Ber.*, **21**, 88—89).—By the action of phenylhydrazine on the chloroform or ethereal solutions of the bibasic anhydrides, the corresponding phenylhydrazile acids are obtained. The following anhydrides react in this way: maleïc, succinic, citraconic, itaconic, camphoric, phthalic, diphenylmaleïc, phthalic, diphenylmaleïc, and diphenylsuccinic (compare Hötte, Abstr., 1887, 669). J. W. L.

Formation of Orthosulphaminecarboxylic Acids. By C. Fahlberg and R. List (*Ber.*, **21**, 242—248).—The products of the oxidation of orthotoluenesulphonamide under different conditions were examined, and the results show that when the oxidation is carried on in alkaline solutions by potassium ferricyanide (Abstr., 1886, 804), by potassium manganate, and by potassium permanganate, orthosulphaminebenzoic acid is formed; that when it is carried on in neutral solutions by permanganate, benzoic sulphinide is the chief product, a small quantity of orthosulphaminebenzoic acid being also formed, probably by the action of the alkali produced by the decomposition of the permanganate, since the yield was much diminished by adding acid from time to time to neutralise the alkali formed; and that when it is carried on by permanganate in solutions rendered acid either by hydrochloric acid, or by a current of carbonic anhydride, orthosulphobenzoic acid and potassium nitrate are formed. Benzoic sulphinide is to be regarded as the primary product of the oxidation, since on evaporation with hydrochloric acid it is converted into orthosulphobenzoic acid and ammonia, and on evaporation with potassium hydroxide into orthosulphaminebenzoic acid. Ammonia, alkaline carbonates, and the oxides of the alkaline earths cannot be employed for this purpose; moreover, in the case of barium oxide, the barium salt of the sulphinide is obtained (compare this vol., p. 282).

Orthoparadisulphaminebenzoic acid, [$COOH : SO_2NH_2 : SO_2NH_2 = 1 : 2 : 4$], is obtained either by oxidising orthoparatoluenedisulphonamide with alkaline potassium manganate, or by evaporating sulphaminebenzoic sulphinide with potassium hydroxide. It crystallises in slender, satiny, microscopic needles, melts at 182—183°, is completely decomposed at 250—260°, and is very soluble in water and alcohol, sparingly soluble in ether. The salts of the alkalis and alkaline earths are readily soluble, and those of the metals are sparingly soluble in water. The *barium* salt, with 5 mols. H_2O, crystallises in large, colourless, monoclinic prisms, the *copper* salt, with 2 mols. H_2O, in bright-blue, silky needles, and the *silver* salt in anhydrous, white needles. The *ethyl* salt is identical with that prepared from disulphaminebenzoic acid (Abstr., 1881, 816). For purposes of comparison, the corresponding salts of disulphaminebenzoic sulphinide were prepared; the *barium* salt, with 3½ mols. H_2O, crystallises in granular aggregates of needles, and the *copper* salt, with 4 mols. H_2O, in blue, microscopic needles; the *silver* salt is anhydrous and indistinctly crystalline. W. P. W.

Derivatives of Phenyldibromisobutyric Acid. By A. KÖRNER (*Ber.*, **21**, 276—277).—When α-methylcinnamic acid (m. p. = 78°) dissolved in carbon bisulphide is treated with bromine, *phenyl dibromisobutyric acid*, CHPhBr·CMeBr·COOH, melting at 137°, is obtained. This, when warmed with alcoholic potash, yields *bromophenylcrotonic acid*, CPhBr ⁚ CMe·COOH, which crystallises from water in matted needles, and melts at 124°. If phenyldibromisobutyric acid is boiled with water, *phenylbromhydroxyisobutyric acid* is formed, melting at 148°. In both cases, the yield of the acid is small, the chief product being *phenylbromopropylene*, C_9H_9Br; this is a colourless liquid, of pleasant odour, and boils at 226° with decomposition. When treated with alcoholic potash, it is converted into *phenylallylene*, CPh ⁝ CMe; this is a pale-yellow liquid of unpleasant odour, boils at 185°, and yields with bromine a liquid *dibromide*, which boils at 250—255° with the evolution of much hydrogen bromide, and a solid *tetrabromide*, which crystallises in lustrous plates and melts at 75°. On treatment with an aqueous solution of mercuric chloride, phenylallylene forms a white, amorphous compound,

$$2C_9H_8,3HgO,3HgCl_2,$$

which when heated with hydrochloric acid yields not phenylallylene but phenyl ethyl ketone, COEtPh. W. P. W.

Parisobutylorthohydroxybenzoic Acid. By L. v. DOBRZYCKI (*J. pr. Chem.* [2], **36**, 389—400).—Anhydrous sodium isobutylphenoxide was prepared by adding the exactly equivalent quantity of isobutylphenol (Liebmann, Abstr., 1882, 171) to alcoholic sodium ethoxide, evaporating off the alcohol, and drying the phenoxide at 140—150° in a stream of hydrogen. The dry phenoxide was then treated, under pressure, with carbonic anhydride, which was rapidly absorbed with evolution of much heat, sodium isobutylphenyl carbonate being formed. When this substance was heated for some time at 130—160° it yielded *sodium parisobutylorthohydroxybenzoate.* The free *acid*, $C_4H_9·C_6H_3(OH)·COOH$, is soluble in boiling water, volatile in steam, and crystallises in long, thin, glistening, white needles. It dissolves readily in alcohol, ether, and chloroform. The aqueous solution gives an intense violet coloration with ferric chloride. The metallic salts are not well characterised. The *methyl salt* yields large, colourless prisms, melts at 54°, and boils at 266°. It is easily soluble in alcohol and ether. Cold soda converts it into a white mass probably of the formula $C_4H_9·C_6H_3(ONa)·COOMe$. The *ethyl salt* is a colourless aromatic liquid boiling at 276°. The *phenyl salt* was prepared by heating the acid with phenol at 130°, and adding the requisite quantity of phosphoric chloride in small quantities. It forms long, glistening needles, sparingly soluble in cold ethyl and methyl alcohols, easily in ether, and melts at 68°. Dilute soda does not attack it in the cold, but saponifies it on heating. When heated in a reflux apparatus, carbonic anhydride is evolved, and phenol, isobutylphenol, and *isobutylbenzophenoxide*, $C_{17}H_{18}O_2$, are formed. The latter compound is now being investigated.

When isobutylphenol is treated with phosphoric chloride, *isobutylchlorobenzene* is formed. The oxidation of this compound proved difficult, potassium chromate and sulphuric acid solution being without action, whilst chromic acid in acetic solution caused complete oxidation. When heated for a long time at 190° with dilute nitric acid, however, it yielded parachlorobenzoic acid. Liebmann's isobutylphenol is, therefore, the para-compound, and from analogy and a consideration of its properties there is little doubt that the acid described above has the constitution [OH : COOH : C_4H_9 = 1 : 2 : 4].

L. T. T.

α-Methylcinnamic Acid. By P. Raikow (*Ber.*, **20**, 3396—3397).—In preparing α-methylcinnamic acid (phenylcrotonic acid) by Perkin's method, and recrystallising the product from light petroleum, two acids were obtained having the same composition. The one crystallises in plates melting at 81—82°, the other in needles melting at 74°. When the latter is often recrystallised, it is converted into the acid of higher melting point. The relative amounts of the two acids is influenced by the temperature at which the reaction between the benzaldehyde, propionic acid, and sodium acetate takes place. At 135°, 24 per cent. of the plates and 30 per cent. of the needles are obtained, whilst at 175° only the needles (56 per cent.) are formed. The two acids differ only slightly in solubility. N. H. M.

Benzeneazomalonic Acid. By R. Meyer (*Ber.*, **21**, 118—119).—Benzeneazomalonic acid, prepared from diazobenzene chloride and ethyl malonate, is identical with the phenylhydrazide of mesoxalic acid.

J. W. L.

Action of Phthalic Anhydride on Amido-acids. By L. Reese (*Ber.*, **21**, 277—278).—α-Leucinphthaloic acid (this vol., p. 148) can be obtained by adding the calculated quantity of phthalyl chloride to a boiling solution of leucine in alcoholic potash, and continuing the boiling of the alkaline solution for one minute; on cooling, the potassium salt crystallises in small, slender, concentrically-grouped needles, and yields the acid on treatment with dilute sulphuric acid and extraction with ether.

Phthalyldisarcosine, $C_{14}H_{16}N_2O_6$, is formed when phthalic anhydride (5 parts) is heated at 140—150° with sarcosine (6 parts). It crystallises in lustrous needles, melts at 168°, and is readily soluble in water and boiling alcohol, sparingly soluble in ether, and insoluble in chloroform and light petroleum. A sodium salt could not be prepared, since the compound is decomposed into its constituents by the action of alkalis; a similar decomposition also occurs when it is heated with concentrated hydrochloric acid. W. P. W.

Azotoluenesulphonic Acid. By J. V. JANOVSKY (*Ber.*, **21**, 119—122).—By appropiate manipulation, it is possible to directly sulphonate azotoluene.

Azotoluenesulphonic acid,

$C_6H_4Me{\cdot}N_2{\cdot}C_6H_3Me{\cdot}SO_3H$ [$Me : N_2 : Me : SO_3H = 4 : 1 : 4 : 3$],

is obtained by the action of fuming sulphuric acid on parazotoluene, care being taken that the temperature is kept below 100°; the best result is obtained by the employment of an acid containing about 24 per cent. SO_3, when the temperature produced by the reaction does not exceed 80°. It crystallises with 5 mols. H_2O in orange-red tables, sparingly soluble in cold water. The potassium (with 5 mols. H_2O), sodium ($4\frac{1}{2}$ mols. H_2O), calcium, barium (11 mols. H_2O), lead and zinc salts are described. When nitrated, it yields a *nitro*-acid, $NO_2{\cdot}C_{14}H_{12}N_2{\cdot}SO_3H + H_2O$, crystallising in small, yellow needles, readily soluble in hot water; several salts were prepared. The corresponding *amido*-acid crystallises in pale-yellow needles, and together with the hydrazo-acid also obtained, will be described later. A *bromo*-acid, $C_{14}H_{12}BrN_2{\cdot}SO_3H$, was prepared, crystallising in tufts of long needles; the potassium and calcium salts are described. Proof of the constitution assigned above to the sulphonic acid is obtained when it is treated with tin and hydrochloric acid, paratoluidine hydrochloride, and paratoluidineorthosulphonic acid [$Me : SO_3H : NH_2 = 1 : 2 : 4$] being formed. A. J. G.

Ethylindole. By A. PICTET and L. DUPARC (*Ber.*, **20**, 3415—3422).—*3′-Ethylindole* is prepared as follows:—30 grams of aniline is added to 50 grams of zinc chloride, and the whole mixed with 35 grams of lactic acid; 200 to 300 grams of sand being added to prevent frothing. It is then heated in a copper retort. The oily products of several fractions are united, dissolved in ether and shaken with small amounts of dilute hydrochloric acid until no more basic substance is dissolved; the ethereal solution is then distilled. It is a bright yellow oil, boiling at 282—284° (corr.), very sparingly soluble in water, readily soluble in alcohol, ether, benzene, and chloroform, &c.; it distils readily with steam. When the alcoholic solution is treated with hydrochloric acid and a chip of pine, it gives an intense red colour. The solution in chloroform gives, on addition of a few drops of a dilute solution of bromine in chloroform, an intense violet coloration, resembling that of potassium permanganate. The picrate melts at 143°. Ethylindole resembles scatole in its general behaviour.

The basic substance formed in the preparation of ethylindole is quinaldine (compare Wallach and Wüsten, *Ber.*, **16**, 2067).

Propionylorthotoluidine, $C_6H_4Me{\cdot}NH{\cdot}COEt$ [$Me : NH{\cdot}COEt = 1 : 2$], is readily obtained by boiling orthotoluidine with propionic acid for six hours. It crystallises from benzene in white needles an inch long, melts at 87°, and is readily soluble in alcohol, ether, and glacial acetic acid, &c., sparingly soluble in hot water. It boils at 298—299° (corr.) under 730 mm. pressure. When oxidised with potassium permanganate, it is converted into *propionylorthamidobenzoic* acid, $COOH{\cdot}C_6H_4{\cdot}NH{\cdot}COEt$. This crystallises from water in white, flat needles, melts at 117°, decomposes at 180° and is readily soluble in alcohol, ether, and in hot water. The *silver salt* crystallises from water in small, white needles. N. H. M.

Dimethylindole. By L. Wolff (*Ber.*, **21**, 123—126).—Aniline reacts with β-bromolævulinic acid, forming dimethylindole, $C_{10}H_{11}N$. The vapour-density shows that this is the product of the reaction and not a compound of twice this molecular formula, as the author suggested in a former paper (Abstr., 1887, 464—465). This indole is identical in all respects with the 2′.3′ dimethylindole obtained by E. Fischer (Abstr., 1887, 149). J. W. L.

Isatoic Acid. By G. Schmidt and E. v. Meyer (*J. pr. Chem.*, [2], **36**, 370—389).—When isatoic acid is heated in closed tubes at 100° with excess of ethyl alcohol, *hydrogen ethyl carboxylanthranilate*, $COOEt{\cdot}C_6H_4{\cdot}NH{\cdot}COOH$, is formed. It crystallises in thin, colourless needles, melts at 126°, and is soluble in boiling water. When heated with hydrochloric acid in closed tubes at 150,° this substance yields carbonic anhydride, ethyl chloride and anthranilic acid hydrochloride. The salts of this acid are crystalline; the *silver salt*,

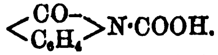
$$COOEt{\cdot}C_6H_4{\cdot}NH{\cdot}COOAg,$$

forms white, microscopic needles or prisms, which are soluble in alcohol and sensitive to light.

When methyl alcohol is substituted for ethyl alcohol in the above reaction *hydrogen methyl carboxyanthranilate*, $COOMe{\cdot}C_6H_4{\cdot}NH{\cdot}COOH$, is formed. This crystallises in minute needles, soluble in boiling water and melting at 176°. The *silver salt* forms small needles which are less stable than the ethyl compound. When heated with hydrochloric acid at 120°, the methyl compound dissolves, but on cooling crystallises out again unchanged. When heated at 200° with an indifferent substance, such as glycerol, carbonic anhydride is evolved, and methyl anthranilate is formed.

With phenol at 180°, isatoic acid yields *phenyl anthranilate*, $NH_2{\cdot}C_6H_4{\cdot}COOPh$, but no carboxyl-derivative. The phenyl salt crystallises in colourless needles melting at 70°. It is easily soluble in alcohol and in ether, sparingly so in boiling water. It is slightly volatile in a current of steam.

When warmed with freshly precipitated ferrous hydrate in the presence of excess of soda, isatoic acid is reduced to anthranilic acid. With zinc-dust and acetic acid, isatoic acid yields anthranilcarboxylic acid,



$$<\begin{matrix}CO-\\C_6H_4\end{matrix}>N{\cdot}COOH.$$

When isatoic acid is heated with glacial acetic acid, carbonic anhydride is evolved, and a compound of the formula $C_{35}H_{27}N_5O_8$ formed. This substance is almost insoluble in the usual solvents, and only melts at a very high temperature. At 150°, it is soluble in ammonia, but crystallises out again unchanged on cooling. With hydrochloric acid at 190°, it yields anthranilic acid hydrochloride. It dissolves in cold concentrated sulphuric acid with slight darkening, but is reprecipitated unchanged on the addition of water. 50 per cent. sulphuric acid at 160° converts it into anthranilic acid. The compound is probably formed from 5 mols. of isatoic acid by the separation of 4 mols. of water. If acetic anhydride is used in place of acetic acid, carbonic anhydride is evolved, and acetylanthranilic acid is formed.

Meyer has already pointed out (Abstr., 1885, 666) that anthranilcarboxylic acid is formed from isatoic acid by oxidising as well as by reducing agents.

From a careful consideration of all the experimental results obtained, the authors conclude that isatoic acid is really identical and not isomeric with anthranilcarboxylic acid, and that the seeming differences of properties are due to the presence in isatoic acid of small quantities of a yellow-coloured impurity. This impurity, which modifies the properties of the acid, is not removed by the ordinary methods of purification, but is destroyed by strong oxidising or reducing agents.

Finally, the authors are inclined to think that the ethyl-compound described above is perhaps identical with that obtained by Weddige by the action of ethyl chlorocarbonate on anthranilic acid, in which case its constitution would be $COOH\cdot C_6H_4\cdot NH\cdot COOEt$, and that of the methyl-compound analogous to it. L. T. T.

Action of Glyoxal on Aromatic Amines. By O. HINSBERG (*Ber.*, **21**, 110—118).—It is easy to obtain reactions between aromatic monamines and glyoxal, if, instead of employing the latter in the free state, its compound with sodium hydrogen sulphite is used.

Anilidoacetanilide, $NHPh\cdot CH_2\cdot CO\cdot NHPh$, is prepared by heating aniline and glyoxal sodium hydrogen sulphite with dilute alcohol in the water-bath for 20 to 30 hours. The melting point, 112—113°, is found to be rather higher than has previously been stated. Under like conditions, paratoluidine gives paratoluidoacetotoluide.

When β-naphthylamine is heated with glyoxal sodium hydrogen sulphite in alcoholic solution, the reaction takes another course and the sodium salt of β-naphthoxindolesulphonic acid separates. The free acid could not be obtained. The potassium salt, $C_{12}H_8N\cdot SO_3K$, crystallises in white plates, and when heated with aqueous hydrochloric or sulphuric acid at 80—90° yields β-naphthoxindole whilst much sulphurous anhydride is evolved.

β-Naphthoxindole, $C_{10}H_6<\substack{NH\\CH_2}>CO$, crystallises in pale green needles, melts at 234°, and is sparingly soluble in water, readily in alcohol, ether, and glacial acetic acid. It dissolves in potash without decomposition, and is insoluble in mineral acids, but with concentrated sulphuric acid it gives a bluish-green coloration which disappears on dilution. The isonitroso-compound, $C_{10}H_6<\substack{NH\cdot CO-\\C(NOH)}>$, prepared by the action of nitrous acid, forms slender, reddish-yellow needles, and melts at 240°.

β-Naphthisatin, $C_{10}H_6<\substack{NH\\CO}>CO$, is prepared by reducing isonitroso-β-naphthoxindole in dilute alcoholic solution by zinc and hydrochloric acid, and treating the colourless liquid so obtained with ferric chloride. It forms slender, red needles, melts at 248°, is moderately soluble in the ordinary solvents, and resembles isatin in its chemical behaviour.

From α-naphthylamine, the corresponding α-compounds were obtained in similar manner. The sodium and silver salts of α-naphthindolesulphonic acid were prepared, but the free acid could not be obtained.

α-Naphthoxindole crystallises in colourless needles, melts at 245°, is insoluble in aqueous soda, and gives a greenish-black coloration with ferric chloride and hydrochloric acid. The isonitroso-compound forms yellowish-red needles, sinters, and turns black at 230°, and is completely fused at 260°.

α-Naphthisatin forms red needles, melts at 255°; the phenylhydrazide melts at 268—270°. Neither of the naphthisatins give the blue coloration with sulphuric acid and benzene containing thiophen. A. J. G.

Condensation-compounds of Metanitrobenzaldehyde with Benzene and Toluene. By O. Tschacher (*Ber.*, **21**, 188—191).—*Metanitrotriphenylmethane*, $CHPh_2 \cdot C_6H_4 \cdot NO_2$, is formed when a solution of metanitrobenzaldehyde in benzene is shaken with half its volume of sulphuric acid; it crystallises from light petroleum in colourless crystals, and melts at 90°. When reduced in acetic acid solution with zinc-dust, it yields the *amido*-derivative, which crystallises from ether in short needles, melts at 120°, and forms a *hydrochloride*,

$$C_{19}H_{15} \cdot NH_2,HCl.$$

The *acetyl*-derivative, $C_{19}H_{15} \cdot NHAc$ crystallises in colourless, nacreous scales, melts at 115°, and is soluble in alcohol.

When metanitrotriphenylmethane in carbon bisulphide solution is treated with the calculated quantity of bromine and exposed to sunlight, an oil, probably $C_{19}H_{14}Br \cdot NO_2$, is obtained which on treatment with potassium acetate in acetic acid solution, and subsequent hydrolysis with aqueous potash, yields *metanitrotriphenyl carbinol*,

$$NO_2 \cdot C_{19}H_{14} \cdot OH.$$

This crystallises from light petroleum in colourless crystals, and melts at 75°; when reduced, it is converted into the *amido*-derivative, which crystallises from ether in colourless, stellate forms, melts at 155°, and yields an *acetyl*-derivative, $OH \cdot C_{19}H_{14} \cdot NHAc$, crystallising in colourless, nacreous scales and melting at 164°.

Metanitrophenylditolylmethane, $CH(C_6H_4Me)_2 \cdot C_6H_4 \cdot NO_2$, is obtained by treating a solution of metanitrobenzaldehyde in toluene with sulphuric acid in the cold. It crystallises from light petroleum in colourless forms, and melts at 85°. W. P. W.

Action of Dichlorether on Phenol. By J. Wislicenus and H. Reinhardt (*Annalen*, **243**, 151—165).—Dichlorether acts on phenol, forming *ethenyltriphenol*, $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{\cdot}(C_6H_4{\cdot}OH)_2$, and other products. If less than 3 mols. of phenol are taken, an insoluble resin is formed. The crude product is dissolved in alkali, reprecipitated by hydrochloric acid, and distilled in a current of steam to remove the excess of phenol. These three operations must be repeated several times. Ethenyltriphenol yields a triacetate soluble in ether, alcohol, chloroform, acetone, benzene, aniline, phenol, and acetic acid. The acetic acid solution is oxidised by ferric chloride, yielding *isorosolic acid*, $C_{20}H_{16}O_3$, a dark, carmine-red, amorphous powder. Isorosolic acid yields a sulphonic acid. From an acetic acid solution of isorosolic acid, chromic acid throws down an amorphous insoluble compound containing chromium.

W. C. W.

Action of Dichlorether on the Dihydroxybenzenes. By J. Wislicenus and M. Siegfried (*Annalen*, **243**, 171—192).—*Ethenyltriresorcinol*, $C_2H_3[C_6H_3(OH)_2]_3$, is formed by the action of dichlorether (14 grams) on 33 grams of resorcinol dissolved in 300 grams of benzene. It is a pale-red, amorphous powder soluble in water, alkalis, alcohol, acetone, and in strong acetic acid. It is precipitated by hydrochloric acid from alkaline solutions, and after the precipitate has been dried in a vacuum, it is sparingly soluble in water, alcohol, and acetic acid. A monacetic derivative is obtained by the action of glacial acetic acid at 85°. It is insoluble in the ordinary solvents, and is converted into an insoluble hexacetate by the action of acetic anhydride at 200°. By the action of acetic anhydride on ethenyltriresorcinol at 170°, an amorphous hexacetate is obtained which is soluble in acetone, chloroform, benzene, and acetic acid. A chocolate-coloured, amorphous substance is formed by boiling ethenyltriresorcinol with glacial acetic acid and ferric chloride. When freshly prepared, it is soluble in alcohol, acetone, and acetic acid. It also dissolves in alkalis, yielding a cherry-red solution. It yields a pentacetate, $C_{20}H_{11}(Ac)_5O_6$. When bromine acts on ethenyltriresorcinol, two hydrogen-atoms are eliminated and six are substituted by bromine, yielding $C_{20}H_{10}Br_6O_6$, a substance soluble in alcohol, ether, acetone, chloroform and acetic acid.

Ethenyltricatechol is obtained as an amorphous compound by the action of dichlorether on a mixture of pyrocatechol and benzene. It is soluble in alcohol, acetone, acetic acid, and alkalis. It yields a hexacetate. On oxidation with ferric chloride, it loses two atoms of hydrogen, but the product could not be obtained in a pure state, although its pentacetate, $C_{20}H_{11}(Ac)_5O_6$, was prepared. Bromine converts ethenyltricatechol into the hexabromide, $C_{20}H_{11}Br_6O_6$, from which the pentacetate, $C_{20}H_6Br_6Ac_5O_6$, was obtained.

Ethenyltriquinol is prepared by the action of dichlorether on a solution of quinol in warm ethyl acetate. It is an amorphous substance, soluble in alcohol, acetone, acetic acid, and in alkalis. The hexacetate is soluble in acetone, chloroform, and acetic acid. Ethenyltriquinol yields a green colouring matter, $C_{20}H_{16}O_6$, when it is treated with ferric chloride; a bromide, $C_{20}H_7Br_9O_6$, can also be prepared. When an excess of dichlorether acts on a solution of quinol in ethyl acetate, a resin and a soluble compound are formed. The latter resembles ethenyltriquinol, but has the composition $C_{16}H_{13}ClO_4$.

W. C. W.

Action of Sulphur on the Salts of Aromatic Hydroxy-compounds. By M. LANGE (*Ber.*, **21**, 260—264).—When β-naphthol is dissolved in aqueous soda and boiled with an excess of sulphur, the latter dissolves and *dihydroxydinaphthyl disulphide*, $S_2(C_{10}H_6\cdot OH)_2$, is formed. This crystallises in white, opaque needles, melts at 210° (uncorr.) and is insoluble in water, sparingly soluble in ethyl alcohol, readily soluble in acetic acid, benzene, amyl alcohol, alkalis, and alkaline sulphides. From the mother-liquors, a second compound of like composition can be separated, which crystallises in long, yellow needles, melts at 168—170°, is more soluble in all solvents than dihydroxydinaphthyl disulphide, and is also distinguished from it by its greater acidity. Both compounds yield β-naphthol on distillation and when heated with alkalis or ammonia at 150°. Dihydroxydinaphthyl disulphide is alone formed when β-naphthol is heated with sulphur and lead oxide at 180—200°.

Resorcinol, when treated in like manner, yields a compound, $C_6H_4O_2S_2$, provisionally termed thioresorcinol. It is a yellow powder, which carbonises before fusion, and is almost insoluble in the ordinary solvents, but readily soluble in alkalis, alkaline carbonates, and alkaline sulphides.

W. P. W.

Action of Fuming Sulphuric Acid on α-Naphthylamine Hydrochloride. By R. MAUZELIUS (*Ber.*, **20**, 3401—3404).—The sulphonic acid prepared by Witt (Abstr., 1886, 554), by the action of fuming sulphuric acid on α-naphthylamine hydrochloride, is shown to be α-amidonaphthalenesulphonic acid. The acid was prepared exactly as described by Witt (*loc. cit.*), and was purified by means of the calcium salt. The different results obtained by Witt appear to be due to the presence of some impurity.

N. H. M.

α-Naphthaldehyde. By E. BAMBERGER and W. LODTER (*Ber.*, **21**, 256—260).—When equimolecular proportions of α-naphthabenzylamine hydrochloride and sodium nitrite are dissolved in water, the *nitrite* of the base, $C_{10}H_7\cdot CH_2\cdot NH_2,HNO_2$, is obtained; this crystallises from water, in which it is sparingly soluble, in long, slender prisms, and melts and suddenly decomposes at 148·5°.

α-Naphthabenzyl alcohol, $C_{10}H_7\cdot CH_2\cdot OH$, is prepared by diazotising the amine. It crystallises in long, lustrous needles, melts at 59—60°, boils at 301° (corr.) under 715 mm. pressure, and is readily soluble in alcohol and ether, less soluble in hot water. On oxidation with potassium dichromate and sulphuric acid, it is converted into *α-naphthaldehyde*, $C_{10}H_7\cdot CHO$. This is a thick, pale-yellow oil of slightly aromatic odour, which boils at 291·6° (corr.) without decomposition and gives the characteristic aldehyde reactions; the *phenylhydrazide* crystallises in lustrous, bright-yellow scales and melts at 185°. On treatment with nitric acid (sp. gr. = 1·47) at − 5—0°, a mixture of nitraldehydes is obtained, one of which crystallises in lustrous, pale-yellow needles, melts at 136°, is very sparingly soluble in cold alcohol, and does not give a colour reaction with acetone and aqueous soda. α-Naphthaldehyde could not be obtained by distilling calcium α-naphthoate with calcium formate. W. P. W.

1 : 4′ Bromonaphthalenesulphonic Acid. By R. MAUZELIUS (*Ber.*, **20**, 3404—3407).—1 : 4′ Bromonaphthalenesulphonic acid (Darmstädter and Wichelhaus, *Annalen*, **152**, 303) is prepared by adding 1 : 4′ diazonaphthalenesulphonic acid to warm, strong hydrobromic acid; the solution is neutralised with potassium carbonate, the potassium salt recrystallised from hot water, dried and rubbed with phosphorus pentachloride; the product is then treated with water, extracted with ether, and crystallised from glacial acetic acid. The chloride is heated with water at 130°. The impure acid melts at 126°. The *barium salt* (with 2 mols. H_2O) is sparingly soluble; the *silver salt* crystallises in pale-yellow lustrous scales. The chloride crystallises in well-formed crystals melting at 94°. The amide forms yellowish needles melting at 232—233°. The *ethyl salt* crystallises well, dissolves readily in alcohol, chloroform, and ether, &c., and melts at 51° (compare also Jolin, *Verhand. d. schwed. Akad. d. Wissens.*, 1877, No. 7). N. H. M.

Reduction of the Thiamides of Aromatic Acids. By E. BAMBERGER and W. LODTER (*Ber.*, **21**, 51—56).—When an aromatic thiamide is reduced with zinc and hydrochloric acid, a benzylamine base is not the only product, a hydrocarbon is obtained at the same time in quantities of about 1 to 2 per cent. of the thiamide employed.

Symmetrical *di-α-naphthylethane*, $C_{10}H_7{\cdot}CH_2{\cdot}CH_2{\cdot}C_{10}H_7$, is formed in the reduction of α-naphthothiamide in alcoholic solution; on evaporation, an oily resinous mass is obtained; this is treated with soda, and the oil which separates is distilled. As soon as the naphthobenzylamine has passed over, the thermometer rises rapidly above 360° and a thick yellow oil distils, and in a short time solidifies. The dinaphthylethane thus obtained, after purification and crystallisation from alcoholic benzene, forms shining, hexagonal plates which are readily soluble in benzene and chloroform, less so in ether, and sparingly soluble in alcohol with a green fluorescence. The crystals are greenish-yellow, and melt at 160° to a yellow oil with moss-green fluorescence.

Symmetrical *di-β-naphthylethane* is obtained by extracting with benzene the resinous product formed in the reduction of β-naphthothiamide. It crystallises from benzene and chloroform in shining silver-white, plates melting at 253°, is only sparingly soluble in ordinary solvents, most readily in chloroform and benzene, and less so in boiling alcohol and ether; the solutions have a blue-violet fluorescence.

The resinous product formed in the reduction of benzothiamide contains *stilbene*, which can be isolated by boiling with alcoholic potash and then distilling with steam. F. S. K.

Action of Dichlorether on Naphthol. By J. WISLICENUS and G. ZWANZIGER (*Annalen*, **243**, 165—171).—*Ethenyltri-α-naphthol* is formed by the action of dichlorether on α-naphthol. The crude product is purified by solution in alkalis and reprecipitation by acetic acid. It is an amorphous, white powder, soluble in acetic acid, alcohol, ether, acetone, and in dilute alkalis. It forms a crystalline triacetyl-derivative, $C_{32}H_{21}Ac_3O_3$. When ethenyltri-α-naphthol is oxidised by ferric chloride, it is converted into a brownish-red colouring matter of the composition $C_{32}H_{22}O_3$. The action of dichlorether on β-naphthol is not analogous to its action on α-naphthol. The product, $C_{22}H_{15}ClO$, crystallises in plates melting at 174°. It resists the action of boiling potash and is not attacked by acetic anhydride. W. C. W.

Terpenes and their Derivatives. By J. W. BRÜHL (*Ber.*, **21**, 145—179).—A comparative study of the chemical and physical properties of the terpenes. A table containing the boiling point, rotation, density *d*, refractive index for the C line *n*, specific refraction $\frac{n^2 - 1}{(n^2 + 2)d}$, and molecular refraction $\frac{n^2 - 1}{n^2 - 2}\frac{P}{d}$ (P being the molecular weight), of a number of the best known terpenes, has been compiled from the data of different observers. The terpenes are thus divided into eight groups, similar to those given by Wallach (Abstr., 1887, 965), phellandrene and terpinene coming under the heading laurene, and menthene and sesquiterpene forming an extra group. These groups are :—

1. *Citrene* (limonene), boiling point 172—179°, the differences probably due to impurities in the specimens examined. Dextrorotatory. Sp. gr. 0·846. Refractive index 1·47. Specific refraction 0·328. Absorbs 2 mols. HCl, the resulting product being identical with the similar product from dipentene, and giving the latter and not citrene when the hydrogen chloride is removed by means of aniline. From this, and the formation of a tetrabromide melting at 104°, the presence of two unsaturated or double bonds is probable, as also from the molecular refraction which agrees closely with that calculated for such an unsaturated compound.

2. *Dipentene.*—Differs from the above only in being optically inactive and yielding a tetrabromide melting at 124°.

3. *Isopentene.*—Dextrorotatory, differs only slightly from the two former in physical properties.

4 *Sylvestrene.*—Has probably never been prepared in a state of purity, and does not appear to differ in any marked degree from the foregoing.

5. *Pinene.*—Boiling point 155—160°. Sp. gr. 0·859. Refractive index 1·463. Specific refraction 0·320. The molecular refraction is that of a compound containing one double bond. This agrees with the chemical evidence, as pinene combines with 2 mols. of bromine and 1 mol. HCl.

6. *Laurene and Menthene.*—Boiling point 173—175°. Lævorotatory. Resembles pinene in other respects.

7. *Camphene.*—Solid, melting at 47°; boils at 156—157°. The hydrogen chloride derivative is very unstable and is decomposed by water at ordinary temperatures; it is therefore probable that this is only a molecular compound, camphene containing no double bond, a view supported by its optical properties.

8. *Sesquiterpene*, $C_{15}H_{24}$.—Found in volatile oils associated with the

terpenes. Boiling point 250—260°. Rotation differs for different varieties. From its optical and chemical properties appears to contain two double bonds.

The author regards the terpenes as derivatives of paracymene. Formulæ similar to those of Wallach (*loc. cit.*) are proposed for citrene, dipentene, pinene, and phellandrene, and a discussion of the various possible formulæ for the other terpenes is entered into.

H. C.

Specific Rotation of Dextrocamphoric Acid and its Salts. By W. Hartmann (*Ber.*, **21**, 221—230).—The specific rotation of dextrocamphoric acid and its salts in solution is represented generally by $[\alpha] = a + bp$ or $A + Bq$, p being the percentage of active substance, q that of the solvent, a the specific rotation for greatest dilution, A that for greatest concentration. The rotation of the free acid in acetic acid, acetone and alcohol varies with the nature of the solvent. The anhydride is optically inactive. The constants in the above equations were determined for solutions of the lithium, magnesium, ammonium, calcium, sodium, potassium and barium salts. By the aid of these constants, the specific rotation of the acid in the salts was calculated, which is more than double that of the free acid, and is nearly equal for all salts for the same dilution. The molecular rotation $M = [\alpha]P/100$, where P is the molecular weight, was also calculated for solutions of the above salts for $p = 0, 5, 10, 15$, and 20. It is found that the molecular rotation is very nearly the same for all salts at the same concentration. Hence also the specific rotation increases with the molecular weight. H. C.

Alantic Acid and Alantole. By Marpmann (*Arch. Pharm.* [3], **25**, 826—827; from *Bresl. ärztl. Zeit.*, **5**, 1887).—On distilling the root of *Inula helenium* with water, a distillate is obtained containing helenin, $C_{12}H_{16}O_2$, alantic anhydride, $C_{15}H_{20}O_2$, and alantole, $C_{20}H_{32}O$.

Alantic acid crystallised from alcohol, melts at 91°, and sublimes with loss of the elements of water, becoming alantic anhydride; both compounds are insoluble in water, soluble in alcohol, and with alkalis form salts soluble in water. *Alantole* is an aromatic liquid which boils at 200°, is lævorotatory, and has ozonising properties somewhat similar to those of the turpentine oils. Helenin, alantic acid, and alantole are antiseptics. J. T.

Oxidation of 1-Quinolinesulphonic Acid. By H. Zürcher (*Ber.*, **21**, 180—182).—Amidosulphobenzoic acid, [$COOH : NH_2 : SO_3H = 1 : 2 : 3$], is formed in small quantity when 1-quinolinesulphonic acid is oxidised to quinolinic acid by Fischer and Renouf's method (Abstr., 1884, 1049). The yield amounts to about 5 grams from 90 grams of quinoline. W. P. W.

Reactions of the Opium Alkaloïds. By P. C. Plugge (*Arch. Pharm.* [3], **25**, 793—811).—With potassium chromate, solutions of narcotine salts, both cold and warm, give a precipitate of free narcotine. Papaverine in the cold gives a mixture of chromate and free alkaloïd: but with heat free papaverine only. Narceïne in cold saturated solution gives no precipitate, but if hot narceïne chromate and free narceïne come down. Thebaïne gives thebaïne chromate. Codeïne also gives the corresponding chromate, whilst morphine gives chromate and free morphine.

With potassium dichromate, narcotine, papaverine and thebaïne give the corresponding dichromates, narceïne gives the dichromate and free alkaloïd. Codeïne in very dilute solution gives the dichromate; stronger solutions afford precipitates which have not yet been examined. Morphine gives a dirty brown precipitate of variable composition.

With potassium ferrocyanide, narcotine hydrochloride gives free alkaloïd or a mixture of variable composition; the papaverine salt gives $(C_{20}H_{21}NO_4)_4,H_4Cfy$; the narceïne salt gives free alkaloïd, the hydroferrocyanic acid becomes free; the thebaïne salt gives the compound $(C_{19}H_{21}NO_3)_4,H_4Cfy$; the codeïne salt solution (1 : 70) is not precipitated; the morphine salt solution (1 : 60) is not precipitated.

With potassium ferricyanide narceïne gives the salt

$$(C_{23}H_{23}NO_7)_6,H_6Cfdy;$$

papaverine and thebaïne give similar precipitates, narceïne gives free alkaloïd, hydrogen ferricyanide also becomes free; codeïne in solution (1 : 70) gives no precipitate; morphine solution (1 : 60) becomes dark coloured and a brown deposit forms after long standing.

J. T.

Quinine Alkaloïds. By O. HESSE (*Annalen*, **243**, 131—150).—Quinine tartrate crystallises with 2 mols. H_2O; it parts with one mol. H_2O at 120°, and the second at 140°. A mixture of quinine and cinchonidine tartrates loses water more easily than quinine tartrate, but if the mixture contains more than 33 per cent. of quinine tartrate, it cannot be thoroughly dried by exposure to a temperature of 120—130°. If ammonia is added to a solution of quinine disulphate containing not more than 10 per cent. of cinchonidine disulphate, ether extracts from the mixture the compound $C_{20}H_{24}N_2O_2 + 2C_{19}H_{22}N_2O$. This substance crystallises in rhombohedra, and is decomposed by boiling ether. On recrystallisation from hot dilute alcohol, crystals of the composition $C_{20}H_{24}N_2O_2 + 7C_{19}H_{22}N_2O$ are obtained. The compound $C_{20}H_{24}N_2O_2 + 2C_{19}H_{22}N_2O$ forms a normal sulphate crystallising with 18 mols. H_2O, a normal tartrate containing 6 mols. H_2O, and a normal chromate with 18 mols. H_2O.

The estimation of quinine as chromate as proposed by de Vrij (Abstr., 1887, 404) is open to several objections (*loc. cit.*).

The author confirms the existence of the compound of quinine and conchinine described by Wood and Barret (*Chem. News*, **45**, 6) and he succeeded in preparing a similar compound of quinine and hydroconchinine, $C_{20}H_{24}N_2O_2,C_{20}H_{26}N_2O_2 + 2\frac{1}{2}H_2O$.

With cinchonidine and homocinchonidine, piperonylic acid forms salts crystallising in needle-shaped crystals soluble in chloroform. The hydrocinchonidine salt is soluble in water and in chloroform. Quinine sulphate is converted into *isoquinine* by solution in strong sulphuric acid. The new base forms a normal sulphate which crystallises in small needles. It does not yield a precipitate with sodium tartrate. *Isoconchinine* is deposited from ether in needles. The sulphate, $(C_{20}H_{24}N_2O_2)_2,H_2SO_4 + 8H_2O$, is crystalline, and the platinochloride, $C_{20}H_{24}N_2O_2,H_2PtCl_6 + 3H_2O$, is amorphous. *Isocinchonidine* crystallises in colourless plates, freely soluble in ether and chloroform. It melts at 235°. *Isocinchonine* is freely soluble in ether. On evaporation, the ethereal solution leaves an amorphous residue which soon becomes crystalline.

Hydroconchinine yields a crystalline sulphonic acid,

$$C_{20}H_{25}N_2O_2\cdot SO_3H + 5H_2O.$$

W. C. W.

Optical Isomerides of Cinchonine. By E. JUNGFLEISCH and E. LEGER (*Compt. rend.*, **105**, 1255—1258).—Pure cinchonine dissolved in four times its weight of a mixture of equal parts of water and sulphuric acid of sp. gr. 1·84, yields a colourless solution which boils at 120°. After boiling for 48 hours, the liquid is amber-coloured, but does not become turbid on cooling. When diluted and made alkaline with sodium hydroxide, it yields an abundant curdy precipitate which soon changes to a porous mass, and gradually hardens. This product contains neither cinchonine nor cinchonicine, but consists of six bases, four of these are isomerides of cinchonine, which form readily crystallisable salts.

Cinchonibine is insoluble in ether but crystallises from boiling alcohol in prismatic needles. It yields a succinate which forms bulky crystals slightly soluble in cold water. It is dextrogyrate, $[\alpha]_D = +175·8°$, in an alcoholic solution of 0·75 per cent.

Cinchonifine is insoluble in ether, but crystallises from boiling alcohol in highly refractive needles. It is dextrogyrate, $[\alpha]_D = +195·0°$, in an alcoholic solution of 0·75 per cent. The succinate crystallises in needles, and is very soluble.

Cinchonigine is soluble in ether, from which it crystallises in prisms, and is lævogyrate, $[\alpha]_D = -60·1°$, in an alcoholic solution of 1 per cent. It yields a distinctly crystalline hydrochloride slightly soluble in water.

Cinchoniline is soluble in ether, and forms very bulky crystals. It is dextrogyrate, $[\alpha]_D = +53·2°$, in an alcoholic solution of 1 per cent. The hydrochloride forms large crystals which are very soluble; the dihydriodide is insoluble. These four compounds increase the number of isomerides of the composition $C_{19}H_{22}N_2O$ to seven.

The other two bases are isomeric one with another, but belong to another group. They are products of oxidation produced with intermediate formation of a sulphonic derivative which is decomposed by water.

α-Oxycinchonine, $C_{19}H_{22}N_2O_2$, forms prismatic needles insoluble in ether but soluble in dilute alcohol. It is dextrogyrate, $[\alpha]_D = +182·56°$, in an alcoholic solution of 1 per cent. Its salts with the hydracids are only slightly soluble.

β-Oxycinchonine, $C_{19}H_{22}N_2O_2$, is insoluble in ether, but dissolves in dilute alcohol, and crystallises in needles arranged in spherical groups. It is dextrogyrate, $[\alpha]_D = +187·14°$, in an alcoholic solution of 1 per cent. Its salts with hydracids are very soluble. C. H. B.

Cocaïne. By A. EINHORN (*Ber.*, **21**, 47—51).—The ethereal salts of benzoylecgonine can be obtained by passing hydrogen chloride into its alcoholic solution; the ethyl, propyl, and isobutyl salts were prepared in this way; they have already been described by Merck (Abstr., 1886, 163).

Succinic acid is formed when anhydroecgonine or ecgonine is oxidised with potassium permanganate; 10 grams of ecgonine hydrochloride yield about 2·2 grams of succinic acid. Ecgonine hydrochloride also gives succinic acid when it is boiled for some time with nitric acid; from 2 grams of the salt, about 1 gram of succinic acid is obtained.

The atomic complex, $C{\cdot}CH_2{\cdot}CH_2{\cdot}C$, which is contained in succinic acid, must originate from the reduced pyridine-ring of the cocaïne-derivative, and the formation of succinic acid shows that the side-chain is either in the α- or β-position.

Nitrogenous compounds are also formed in the oxidation of ecgonine and anhydroecgonine. F. S. K.

Physiological Chemistry.

Behaviour of Congo-red with Human Urine and with Acid Salts. By E. BRÜCKE (*Monatsh. Chem.*, **8**, 632—637, compare Abstr., 1887, 986).—Human urine and a solution of ammonium acetate containing free acetic acid give similar tints with Congo-red. The addition of magnesium sulphate, however, in no way affects the colour of the former, whilst it causes the latter to darken rapidly with the formation of a brownish-black precipitate. The acid tartrates of ammonium and potassium give with Congo-red a beautiful violet colour. The author sees no reason to change the conclusion he draws from previous experiments with Congo-red, that human urine contains no free acid. G. T. M.

Chemistry of Vegetable Physiology and Agriculture.

Colour of Leaves in Relation to the Assimilation of Carbon. By T. W. ENGELMANN (*Ann. Agronom.*, **13**, 477—480; from *Bot. Zeit.*, 1887, 25—29).—The yellow leaves of an elder bush were studied side by side with the green leaves of the same plant by means of Engelmann's microspectral photometer, and by their behaviour towards aërobic bacteria.

The absorption-spectrum of the living yellow cells shows that the bands II and III in the orange and the yellow-green which belong to the green colouring constituent (cyanophyll or pure chlorophyll), and which are absent from the spectrum of xanthophyll, are scarcely indicated.

In the spectrum of the green living cells, on the other hand, these bands are easily identified, although Reinke, working with Glan's photometer, did not succeed in finding them. It would thus appear that the yellow cells contain little chlorophyll proper, or chlorophyllane, and it would be expected that they should lack the power of assimilation. By immersing equal areas cut out of the yellow and green leaves in a liquid charged with aërobic bacteria, and exposing the liquid to the light, it is easily seen that the yellow cells disengage far less oxygen in a given time than the green cells, and hence it is probable that if they contained pure xanthophyll only, the assimilating power would be *nil.*

With reference to the plants in which the light reaches the granules of true green chlorophyll through layers of cells coloured red or purple (copper-beech, red cabbage, &c.), the author observes that they do not differ from what is observed in green plants either in the disposition of the chlorophyll granules or in their size, or the nature or intensity of their colour. Moreover, the red varieties of a plant, for example, *Coleus*, are quite as large and vigorous as the green specimens. It follows that the red colouring matter of these plants can only absorb those rays which have little influence on assimilation.

The colouring matter is always a red-purple, which has most effect in absorbing the green rays, whilst red rays pass freely, and blue and violet very well. The curve of absorption rises about the middle of the spectrum, and descends again at the other end. When the solution is very concentrated a large absorption-band is seen between the wave-lengths $\lambda = 0{\cdot}59\mu$ and $\lambda = 0{\cdot}50\mu$. Speaking generally, the absorption of light is complementary to that caused by solutions of chlorophyll. If, as was formerly believed, the maximum of assimilation corresponded with the yellow rays, that process would be much impeded in the red plants, for the yellow rays are enfeebled to the extent of one-third in passing through the red solution.

J. M. H. M.

Supply of Food Constituents at Different Periods of Plant Growth. By G. LIEBSCHER (*Bied. Centr.*, 1887, 658—660).—As a basis for the science of manuring, the author advances a new theory. The view sometimes held, that one species of plant has a greater power than another of taking up some particular food constituent cannot be reconciled with the laws of osmosis; but the difficulties met with can be explained in another way. Each day the root should supply a certain amount of food to the plant; this amount varies more or less at different stages of growth, and further, these variations differ in the case of different plants; thus one species requires a fairly uniform daily supply throughout its period of growth, whilst another requires much more at one stage than at another. From the composition of various plants at different stages of growth, the author has constructed a number of curves showing how these supplies vary. Such information affords an important clue to the proper manuring of a particular species; thus for a plant requiring a uniform daily supply, a slowly decomposing and lasting manure is appropriate;

whilst an easily soluble one should be given to a plant whose demand is large during a short period. H. H. R.

Wheat Experiments in 1887. By A. LADUREAU and MOUSSEAUX (*Ann. Agronom.*, 13, 538—551).—The experiments were carried out on the poor lands of the Brie district, and had for their object to demonstrate the utility of artificial manures, and to ascertain the most productive and economical manuring for the district. The soil, limed in 1885, contained only 0·084 per cent. N, 0·085 per cent. P_2O_5, 0·325 per cent. K_2O, and 0·280 per cent. CaO.

One variety of wheat (Golden Drop) was sown on all the plots, on the same day, October 11th, 1886, at the uniform rate of 2 hectolitres per hectare; each plot measured 3 ares. Both straw and grain were weighed on each plot, the value calculated out at the price actually realised, and compared with the expense of the various manures used. The yield varied from 950 kilos. per hectare of grain, and 1550 kilos. straw on the unmanured plot, to 3200 kilos. grain and 5650 kilos. straw on the best plot, which was manured with 50 cubic metres farmyard manure, and 300 kilos. of 15 per cent. superphosphate per hectare in the autumn, and top dressed with 250 kilos. sodium nitrate in the spring. The increase obtained on this plot over the unmanured plot exceeded the cost of the manures applied by 319·75 francs per hectare. A still more favourable result (although from a smaller crop) was obtained on the plot dressed with 100·5 kilos. P_2O_5 in superphosphate and 48·5 kilos. of ammoniacal nitrogen per hectare in the autumn, 29·75 kilos. nitrogen as sodium nitrate per hectare in the spring; on this plot, the increase obtained by the manure exceeded the cost of the latter by 389·4 francs per hectare. The results obained on all the plots justify the following conclusions:—

1. Superphosphate applied at the rate of 50 kilos. per hectare produces an increase of crop on these soils.
2. Ammonium sulphate applied in spring gives results greatly superior to those given by the same money value of sodium nitrate.
3. Basic cinder substituted for some of the superphosphate did not give good results. The authors are now trying basic cinder alone, and expect to get better results with it. That employed in the present series of experiments was very coarsely ground.
4. Farmyard manure alone did not even repay its cost, a result probably due to the exceptional drought of the season. The authors recommend the wheat growers of this distrtct to sell their farmyard manure to the vine growers, and with a portion of the proceeds to buy artificial manures. J. M. H. M.

Experimental Culture of Sugar-beet at Grignon in 1887. By P. P. DEHÉRAIN (*Ann. Agronom.*, 13, 529—538).—The experiments were to decide two points, namely, the quality of the seed obtained at Grignon from previous crops of Vilmorin's sugar-beet, and the effect of farmyard manure as compared with mineral manures on the yield of sugar. The plots sown with the Grignon seed were therefore compared with parallel plots sown with seed obtained direct from Vilmorin; the manures tried were farmyard manure, sodium nitrate, and ammonium sulphate; and the quality of the roots from the various plots was ascertained by selecting proportionate numbers of large, medium, and small roots from each plot, and testing the juice by the hydrometer and in the saccharimeter. The chief results of the experiments are that the continuously unmanured plots of both series yielded very small crops of small roots poor in sugar, namely, 13900 and 10100 kilos. of roots per hectare, density of juice 6·9 and 7·2, percentage of sugar in juice 15·8 and 14·6. The mean percentage of sugar in the juice of the roots from the Grignon seeds was 17·7, and in the juice of the roots from the Vilmorin seeds 17·1, so that it is evident a good sample of seed may be relied on by the farmer for at any rate a second harvest. Both series of plots proved that on the light soil of Grignon, moderate dressings of farmyard manure, with or without the addition of sodium nitrate or ammonium sulphate, produced considerably larger crops than the sodium nitrate or ammonium sulphate alone, and that the roots grown with the farmyard manure were by no means poor in sugar, the juice containing 18 to 19·5 per cent.; 30000 kilos. farmyard manure per hectare, or 20000 kilos. with 200 kilos. sodium nitrate, were found to be the best dressings; a larger quantity of farmyard manure diminished the crop, and ammonium sulphate proved, as it generally has done at Grignon, decidedly inferior to sodium nitrate. J. M. H. M.

Iron in Wine. By Sambuc (*J. Pharm.* [5], **16**, 344—345).—A wine from Seyne (Var.) from an American vine, the Jacquez, was found to contain, per litre:—Alcohol, 67·54 grams; dry extract at 100°, 20·50; acidity in terms of sulphuric acid, 6·20; total ash, carbonated, 2·60; anhydrous ferric oxide, 0·11. The iron was determined both gravimetrically and volumetrically. The usual amount of iron in wines is equivalent to 0·01—0·02 gram of ferric oxide.

J. T.

Nitrates in Soils and Water. By E. Bréal (*Ann. Agronom.*, **13**, 561—568).—The author has applied the mode of detecting nitrates described in a previous memoir (Abstr., 1887, 1138) to the study of the arable, pasture, and forest soils, and the waters in the neighbourhood of Baden, Switzerland. A few cubic centimetres of the sulphophenol reagent in a stoppered bottle, and some strips of prepared filter-paper, are sufficient to show that nitrates are abundant in the arable soils, deficient in the meadow soils, and almost absent from the forest soils. He attributes the deficiency in the last two descriptions of soil to the excess of organic matter hindering nitrification, and to the rapid consumption of what nitrates are formed by the perennial crops. The mountain streams are free from nitrates, and so is the water of a hot mineral spring highly charged with sulphate of lime.

J. M. H. M.

Sulphur and Phosphorus in Plants, Soils, and Moulds. By Berthelot and André (*Compt. rend.*, **105**, 1217—1222).—Sulphur may exist in plants, soils, and moulds, in the form of sulphates directly precipitable as barium sulphate; in the form of compounds analogous to the ethyl sulphates from which the sulphur is obtained as sulphate by hydrolysis or oxidation; in the form of salts such as sulphides, sulphites, and thiosulphates, which can be converted into sulphates by oxidation in solution; and in the form of carbon-compounds such as taurine, cystin, albumin, &c., the sulphur in which is not converted into sulphate by oxidation in solution.

In order to estimate the total sulphur or phosphorus, the substance previously dried at 100° is burnt in a current of oxygen in a glass tube, the products of combustion being conducted through a column of pure anhydrous sodium or potassium carbonate. Care must be taken that the temperature does not rise sufficiently high to fuse the alkaline carbonates in the ash. When combustion has ceased, the current of oxygen is continued for some time in order to convert any alkaline sulphides into sulphates. The contents of the tube are dissolved in water, acidified with hydrochloric acid, and precipitated with barium chloride. In the filtrate from the barium sulphate, the phosphorus is precipitated by means of ammonium molybdate, and is afterwards converted into magnesium pyrophosphate.

The soil examined contained 1·418 gram of sulphur per kilo., but 1 per cent. hydrochloric acid only extracted one-seventh of this, and concentrated nitric acid dissolved very little more.

The mould contained 6·156 grams of sulphur per kilo., of which 0·947 gram was soluble in cold dilute hydrochloric acid, and 2·0213 in concentrated boiling nitric acid.

One of the specimens of the plant, *Mercurialis annua*, contained 10·768 grams of sulphur per kilo., 3·040 being soluble in cold dilute hydrochloric acid. Another specimen contained 6·584 grams per kilo., 2·834 grams being soluble in cold 1 per cent. hydrochloric acid and 4·554 in boiling concentrated nitric acid.

The sulphur existing as sulphate is in all three cases only a small proportion of the total quantity, and the sulphur convertible into sulphate by oxidation in solution, although greater, is still only a fraction of the total amount.

Phosphorus may exist in plants, moulds, and soils, as phosphates soluble in water or acids; as ethereal compounds yielding phosphates on hydrolysis or oxidation; as phosphides or phosphites, &c., which can be oxidised to phosphates in solution; and as organic compounds which cannot be converted into phosphates in the wet way.

The soil examined contained 0·641 gram of phosphorus per kilo., 0·134 gram of which was soluble in hydrochloric acid of 1 per cent., 0·420 in hydrochloric acid of 10 per cent., 0·603 in boiling concentrated nitric acid. The total phosphorus is much greater than that existing as phosphate, and it is not completely oxidised by nitric acid.

The mould contained 3·091 gram per kilo., 2·328 being soluble in cold dilute hydrochloric acid, and 3·085 in hot concentrated nitric acid. In this case, the proportion of phosphate is very large, and it is noteworthy that concentrated nitric acid removes the whole of the phosphorus. This last result is, however, probably abnormal.

The first specimen of the plant contained 2·812 grams of phosphorus per kilo., 1·668 gram being soluble in cold dilute hydrochloric acid. The second specimen contained 5·440 gram per kilo., 2·963 being soluble in cold dilute hydrochloric acid, and 4·154 in hot concentrated nitric acid. The proportion of phosphorus depends largely on the age of the plant. The last specimen contains twice as much as the mould, and nine times as much as the soil. The proportion of soluble phosphates is greater than in the soil, and is comparable with that in the mould.

From these results, it is evident that sulphur and phosphorus, like nitrogen, exist in plants, moulds, and soils, in several different forms.

C. H. B.

Analytical Chemistry.

Polaristrobometric Analysis. By H. LANDOLT (*Ber.*, **21**, 191—220).—The specific rotation of nearly all circularly polarising solutions may be expressed in terms of—(1.) The percentage q of the inactive solvent, $[\alpha] = A + Bq + Cq^2$. (2.) The percentage p of the active substance, $[\alpha] = a + bp + cp^2$. (3.) The concentration c, $[\alpha] = A_1 + B_1c + C_1c$. In many cases, the third term may be neglected. The two last equations may be used for either concentration or percentage composition, since $c = pd$, where d is the specific gravity of the solution.

In determining from the rotation the amount of substance in solution, the following cases have to be distinguished:—

I. A solution may contain a single active substance in an inactive solvent. This is the most general case, and the specific rotation is as a rule constant, that is, the angle of rotation is proportional to the concentration, as is the case for aqueous solutions of cane-sugar, milk-sugar, maltose, raffinose, dextrose, lævulose, invert sugar, and galactose. The specific rotation is, however, not always constant, but sometimes a linear function of the concentration, as, for instance, for solutions of nicotine and camphor in alcohol.

II. Solution of an active substance in two inactive solvents. The specific rotation of nearly all active substances being unequally influenced by different solvents, the action of each solvent alone on the rotation has to be separately considered. These will be $[\alpha] = A + Bq$ and $[\alpha]_1 = A + B_1q$, the constant A being the rotation of the pure active substance and the same in each case. Hence if q and q_1 are the weights of two solvents contained in 100 parts of the mixture, the specific rotation will be $[\alpha]_m = A + Bq + B_1q_1$. This presupposes each solvent to act perfectly independently of the other, which, however, only happens in the case of cane-sugar, the rotation of which is the same for all solvents. In other cases, the value of $[\alpha]_m$ lies irregularly between $[\alpha]$ and $[\alpha]_1$, as, for instance, for narcotine in 1 vol. alcohol to 2 vols. chloroform, or it attains a maximum higher than either $[\alpha]$ or $[\alpha]_1$, as for cinchonidine in the above solvents or cinchonidine nitrate and hydrochloride in mixtures of alcohol and water.

III. Solution of two active substances in an inactive solvent.

Firstly, the combined weight of the two substances in 100 c.c. solution may be known. Let the specific rotation of the solution be $[\alpha]$, and the mixture contain x per cent. of one constituent of the specific rotation $[\alpha]_x$, and $y = 100 - x$ of the other constituent of the specific rotation $[\alpha]_y$. Then $[\alpha]_x\, x + [\alpha]_y\,(100 - x) = 100\,[\alpha]$, from which x and y are obtained in terms of $[\alpha]$, $[\alpha]_x$, and $[\alpha]_y$. Instances of this are solutions of cane-sugar and raffinose and quinine and cinchonine sulphates. Secondly, the combined weight of the two active substances may be unknown, and the analysis is then effected by measuring the rotation of the solution, and converting one or both of the constituents into another optically active substance by inversion, and again measuring the rotation. If only one constituent undergoes inversion, if ϕ_1 and ϕ_{11} the angles of rotation for unit concentration of each constituent be known, ρ the rotation of the inverted substance, and c_1 and c_{11} the concentrations required, we have—

$$\begin{aligned} &\text{Before inversion, } \phi_1 c_1 + \phi_{11} c_{11} = \alpha \\ &\text{After inversion, } \rho k c_1 + \phi_{11} c_{11} = \alpha \end{aligned}$$

from which c_1 and c_{11} may be calculated. This is true for solutions of cane-sugar and invert sugar and cane-sugar and dextrin, the cane-sugar being the substance inverted. If both constituents undergo inversion, then if ρ_{11} is the rotation of the second inverted substance—

$$c_1 = \frac{\rho_{11}\alpha - \phi_{11}\alpha_1}{\rho_{11}\phi_1 - \rho_1\phi_{11}} \text{ and } c_{11} = \frac{\rho_1\alpha - \phi_1\alpha_1}{\rho_1\phi_{11} - \rho_{11}\phi_1}.$$

This is true for a solution of raffinose and cane-sugar.

IV. Analysis of inactive substances in solution. This would be effected by measuring the influence of certain inactive substances on substances of known rotation, such, for instance, as the action of boric acid on tartaric acid solutions. Little has been done in this direction, and no attempt at formulating the above influence can at present be made.

H. C.

Correct Analysis of Superphosphates. By J. Ruffle (*J. Soc. Chem. Ind.*, 6, 491—494 and 704—705).—In furtherance of his investigations on moisture and free acid in superphosphates (this vol., p. 87), the author suggests the following method of analysing superphosphates:—(1.) Moisture: estimated by calcium chloride in a vacuum. (2.) Soluble phosphoric acid: estimated by direct determination. (3.) Insoluble phosphate: estimated by direct calculation from the amount of insoluble phosphoric acid after evaporation to dryness with hydrochloric acid and re-solution with hydrochloric acid. (4.) Calcium sulphate: estimated by determining the whole sulphuric acid present and calculating this into anhydrous calcium sulphate. (5.) Sand: estimated by evaporating to dryness with hydrochloric acid and re-solution in hydrochloric acid. (6.) Combined water and organic matters, including the uncombined calcium oxide: estimated by difference. (7.) Alkalis, magnesia: amounts as determined.

By this plan no more work is introduced than is practised at the present time, whilst the statements 1, 2, 3, 4, 5, and 7 will be true from direct determination, and the commercially unimportant "combined water and organic matter" will not be attempted; hence false statements will be avoided.

The author is of opinion that the calcium oxide existing as monocalcium phosphate in ammoniated phosphates may be wholly passed over, and the total calcium oxide, less the amount of the insoluble phosphate, be calculated out to calcium sulphate. D. B.

Separation of Zinc from Nickel and Manganese and Estimation of Nickel. By T. BAYLEY (*J. Soc. Chem. Ind.*, **6**, 499).—A good separation of zinc from nickel and from manganese may be made in a hot solution containing free phosphoric acid by precipitation with hydrogen sulphide. Cobalt has a tendency to go down in small quantity with the zinc. In order to precipitate nickel from solutions, the author recommends the addition of ammonium sulphide until the last drop renders the liquid alkaline; this is followed by ammonium benzoate, and afterwards by a few drops of hydrochloric acid. In this solution, the nickel is completely precipitated as sulphide. The latter is heated in a porcelain dish, dissolved in nitric acid, evaporated, ignited, and weighed as sulphate. The ignition should be effected at a low red heat, and the dish allowed to cool. The sulphate is then treated with sulphuric acid and submitted to a further short ignition. Success would appear to depend on the shortness of the second ignition.

D. B.

Reaction of Iron with Nitric Acid. By T. BAYLEY (*J. Soc. Chem. Ind.*, **6**, 499—500).—When an assay of "nitre" in sulphuric acid is made in the nitrometer, an error is caused by absorption of nitric oxide when the acid contains iron. Nitric oxide, shaken with mercury and pure sulphuric acid, suffers no absorption, nor does mercury pass into solution in the acid unless the acid contains a small quantity of iron. On copiously diluting the acid by the addition of air-free water, and subsequently adding a solution of a ferricyanide to the cooled acid liquid, the blue reaction is readily obtained. The mercury seems to take no part in the reduction of the ferric salt, since the results can be equally well obtained if pure nitric oxide is passed through a set of Geissler bulbs charged with sulphuric acid containing ferric sulphate. The sulphuric acid in this case, as in the nitrometer, assumes a purple tint, which is characteristic of the reaction when it takes place in the acid, but not in the aqueous solution.

D. B.

Action of Oils on Polarised Light. By W. BISHOP (*J. Pharm.* [5], **16**, 300—301).—Besides resin and castor oils, there are two others which very perceptibly affect polarised light. Thus in a tube of 20 cm. long colza oil gave a rotation of $-1{\cdot}6^\circ$ to $-2{\cdot}1^\circ$, and sesame oil gave from $+3{\cdot}1^\circ$ to $9{\cdot}0^\circ$. Of several other vegetable oils examined none gave as much as $1{\cdot}0^\circ$. In the case of certain linseed oils, when found to have dextrorotative power, they should be examined for sesame oil before concluding that resin oil has been added.

J. T.

General and Physical Chemistry.

Dispersion Equivalents. By J. H. GLADSTONE (*Proc. Roy. Soc.*, **42**, 401—410).—This paper is a continuation of the author's researches on dispersion equivalents. Notwithstanding the difficulties of the investigation, the following conclusions have been arrived at:—1. That dispersion, like refraction, is primarily a question of atomic constitution. 2. That dispersion, like refraction, is modified by profound differences of constitution, such as change of atomicity. 3. That dispersion frequently reveals differences of constitution, at present unrecognised. The following dispersion equivalents (H — A) have been determined:—Phosphorus (liquid), 3·0; sulphur (double bond), 2·6; sulphur (single bonds), 1·2; hydrogen, 0·04; carbon, 0·26, 0·51, and 0·66; oxygen (double bond), 0·18; oxygen (single bonds), 0·10; chlorine, 0·50; bromine, 1·22; iodine, 3·65; nitrogen, 0·10; CH_2, 0·34; NO_2, 0·82. The values for CH_2, H, and C are worked out in the same way as the refraction equivalents. In unsaturated compounds, the dispersion equivalent is much greater, (0·5) in allyl compounds and olefines, and at least 0·8 in the aromatic series. Where the carbon has all four bands satisfied with carbon-atoms (with refraction value 6·0), the dispersion equivalent is enormously increased. In considering the dispersion equivalents of solutions of metallic salts, it is pointed out that where the solution is dilute the values are untrustworthy, owing to the smallness of the specific dispersion, the values for potassium and sodium alone are therefore considered. The difference between the dispersion equivalents of their salts is 0·09. In determining the value for potassium itself, the haloïd salt was rejected, as it was anticipated that the chlorine value might be higher than it is in organic compounds, as is the case with the refraction equivalents. Determined from the formate and acetate, with the values given above for carbon, hydrogen, and oxygen, the dispersion equivalent for potassium is 0·53 and 0·44 for the salts respectively. From potassium hydroxide viewed as water, with a hydrogen-atom replaced, the value 0·565 is obtained. From the nitrite, by subtracting the value for NO_2, 0·48 is obtained. From the cyanide, 0·58; from the carbonate, 0·40; from the oxalate, 0·59. These variations cannot be due to experimental error, nor is it probable that potassium has more than one dispersion equivalent, as it has only one refraction equivalent. The uncertainty probably lies in the value of the radicles to which the metal is joined. H. K. T.

Mathematical Analysis of the Spectra of Magnesium and Carbon. By A. GRÜNWALD (*Monatsh.*, 8, 650—712).—In accordance with the principle laid down by the author (Abstr., 1887, 1070), an analysis of the spectra of magnesium and carbon has been effected, the data of different observers, chiefly those of Liveing and Dewar, being used for this purpose.

The magnesium spectrum is found to show the presence of the primary substance *c* in the same condition in which it is found in oxygen and carbon, of the primary substance *b* in the state in which it exists in free hydrogen, and in the more condensed state in which it is found in the water-vapour spectrum, and also of *b* (helium) in an uncondensed state. Besides these, a number of very weak, and at present unknown hydrogen and oxygen lines are present.

The spectrum of carbon contains the primary substance *c* in the state in which it is found in oxygen and magnesium, and also the substance *b*. This latter exists in four different conditions: in the state in which it is observed in free hydrogen; in the state in which it exists in the hydrogen of water-vapour; and in a more dilated chemical condition, and a more condensed condition than that in which it occurs in free hydrogen. A number of hydrogen and oxygen lines are also present, most of them very weak, but which, on multiplying their wave-lengths by the factor $\frac{2}{3}$, as in the case of those in the magnesium spectrum also, are converted into lines in the water spectrum. H. C.

Compounds of the Rare Earths yielding Absorption-spectra. By G. KRÜSS and L. NILSON (*Ber.*, **21**, 585—588).—A rejoinder to Bailey (this vol., p. 208).

Contact Electricity. By W. v. ULJANIN (*Ann. Phys. Chem.* [2], **33**, 238).—The author points out that Exner (this vol., p. 208) has misunderstood his method (*Ann. Phys. Chem.* [2], **30**, 699) of determining the potential difference between zinc and copper, as he appears to have assumed that the author covered a copper cylinder with a zinc one, and inserted such a fraction of a Daniell, that when the latter cylinder was removed there was no deflection of the electrometer. This arrangement would clearly not enable the potential difference to be measured, as it would require that the envelope also should be at the same potential, and the latter is determined by that of the walls of the room.

In the arrangement used, the two cylinders were of zinc, and were surrounded by a copper envelope, and before removing the outer cylinder it was separated from the inner one. Then assuming the two zinc cylinders to be at the same potential, there would be no deflection if the copper envelope was at the same potential. This condition was satisfied by the introduction of a certain fraction of a Daniell in the earth connection of the envelope.

It is clear that the method would not serve to determine any potential difference between the zinc cylinders, as it depends on the assumption that they are at the same potential, being of the same metal, and in contact. G. W. T.

Maximum Galvanic Polarisation of Platinum Electrodes in Sulphuric Acid. By C. FROMME (*Ann. Phys. Chem.* [2], **33**, 80—128).—The great discrepancies between the different determinations of the maximum polarisation in a voltameter containing dilute sulphuric acid with platinum electrodes, induced the author to investigate the circumstances on which the amount of polarisation depends. *A priori*, the polarisation might be expected to depend on the nature of the surface of the electrodes, on their dimensions, on the concentration of the acid, and on the pressure at which the gases are liberated.

The concentration of the acid in the different experiments varied from 0·18 to 65 per cent.

The author finds that the manner in which the amount of polarisation varies with the concentration is most complicated in the case of very dilute solutions, for, as the concentration is gradually increased, the polarisation at first increases and reaches a maximum, and afterwards falls to a minimum; when the anode is small, it passes through a second maximum and minimum, until it finally increases steadily with the concentration; with a larger anode, only a single maximum and minimum are observed.

In very dilute solutions, the amount of polarisation is found to depend on whether the water used is distilled in glass or in metallic vessels, this being doubtless due to the presence of small particles of glass or of metal in the distilled water.

When the cathode is small, its surface becomes blackened by the passage of the current, whilst a larger cathode is not sensibly altered.

With the more dilute solutions, and when both the electrodes were small, a yellow deposit was observed on the anode. The black deposit remains unaltered after treatment with concentrated sulphuric acid, but it is slowly dissolved by aqua regia. It can also be removed by reversing the current for some time, or it can be scraped off. This deposit had already been observed by de la Rive (*Ann. Phys. Chem.*, **41**, 156; **45**, 421) and by Poggendorff (*ibid.*, **61**, 605), and their experiments showed that it consisted of platinum in a state of powder, mechanically detached from the cathode. In some of the experiments, even when the cathode is larger, a greyish-brown deposit was observed on the latter, but only when the water had been distilled in glass vessels, from which the author concludes that it was due to particles of glass. It was easily dissolved by concentrated sulphuric acid.

In the case of the larger anodes, a dark yellow coloration was observed after some time. This yellow deposit on the anodes was unaffected by treatment with hot concentrated sulphuric acid or aqua regia, and it occurred whether the water had been distilled in glass or in metallic vessels. The author was unable to determine its cause, but concluded that it was not due to the presence of any impurity in the solution. The amount of polarisation is found to depend on the size of the electrodes; with dilute solutions, the size of the anode is the more important, with stronger ones that of the cathode.

With the solutions used containing, as previously stated, from 0·18 to 65 per cent. of acid, the E.M.F. of polarisation varied from 1·94 to 2·43 of a Daniell when the cathode and anode were both large; from 1·45 to 2·98 when the cathode was small and the anode large; from 1·90 to 4·18 when both cathode and anode were small; and from 1·89 to 4·31 when the cathode was large and the anode small. The least variation, therefore, occurs when both the electrodes are large, and the greatest when the cathode is large and the anode small.

The resistance of the voltameter when traversed by a strong steady current diminishes as the concentration of the acid increases, and ultimately reaches a minimum value when the concentration is about the same as that for which the conductivity is found to be a maximum by observations with alternate currents; after this, it increases with further increase in the concentration. When, however, the anode is small, the resistance continues to diminish up to the highest limits of concentration used in the experiments. G. W. T.

Electromotive Forces of Metals in Cyanide Solutions. By S. P. Thompson (*Proc. Roy. Soc.*, **42**, 387—389).—The electromotive forces of copper and zinc in cyanide solutions are examined in order to ascertain the cause of the possibility of depositing these two metals simultaneously. It is found that with higher concentration, the E.M.F. of copper increases more than that of zinc; moreover, in a cold dilute solution of potassic cyanide the E.M.F. of zinc is higher than that of copper, whilst in a boiling saturated solution the E.M.F. of copper is greater than that of zinc: hence it is possible to construct a battery consisting of one metal, copper, and one electrolyte, a solution of potassic cyanide, the anode being kept hot and the cathode cold. Tables are given showing the E.M.F.'s of various metals compared with carbon in cyanide solutions of various strengths. Maxima are frequently found at intermediate stages of concentration. In a mixed solution of copper and zinc cyanides, there is a neutral condition, in which the E.M.F.'s of zinc and copper are equal, depending on the relative amounts of metal, the concentration of the solution, and the temperature. The E.M.F. of the copper is the most sensitive, especially to variations in the concentration of the solution. At the cathode, the concentration is determined, on the one hand, by the rapidity with which the metal is deposited, that is, by the current-density; on the other, by the rapidity of diffusion; hence there will be a certain current-density at which the solution will be maintained in the neutral condition and the metals be deposited equally.

H. K. T.

Resolution of the Electromotive Forces of Galvanic Elements. By J. Miesler (*Monatsh.*, 8, 713—720).—In continuation of his work on this subject (this vol., p. 330), the author has examined Marié-Davy, de la Rue, and Niaudet cells, and in each the sum of the potential differences in the various parts of the cell is found to be equal to the total E.M.F. Accumulators were examined, and for these the above was also found to be true. On discharging an accumulator and measuring the potential differences at different intervals, as the total E.M.F. decreased to about one-half of its original value, the potential difference between the negative plate and acid also diminished, but that between the positive plate and acid remained the same. After the cell had been short circuited for some time, the exact opposite had, however, taken place, for the potential difference between the negative plate and acid was still the same, whilst that between the positive plate and acid had decreased. An attempt mechanically to construct an accumulator that should give the same potential differences as a charged accumulator failed. H. C.

Thermal Alteration in a Daniell Cell and in an Accumulator. By G. Meyer (*Ann. Phys. Chem.* [2], **33**, 265—289).—Investigations have been made on the thermal changes in a Daniell cell by Lindig (*Ann. Phys. Chem.*, **123**, 1), Voller (*ibid.*, **149**, 394), and v. Helmholtz (*Ber.*, **18**, 22), and the latter has shown that in a zinc sulphate cell the temperature-coefficient depends on the degree of concentration of the solution. The object of this paper is to determine more fully on what circumstances the temperature-coefficient depends, in the case both of sulphuric and zinc sulphate cells, and to determine whether the temperature-coefficient of the cell is equal to the sum of the temperature-coefficients at each contact of unlike substances.

In order to ensure their purity, the metals used were obtained by electrolytic deposition from copper sulphate and zinc sulphate, and the copper sulphate, zinc sulphate, and sulphuric acid were chemically pure. The metals and liquids composing the cell were contained in a glass tube of special construction, and the liquids were separated by parchment-paper; the dissolved air being got rid of by use of an air-pump. The measurements of the E.M.F. were always made with a quadrant electrometer, so that there was no polarisation, and the electrometer reading was taken directly after the zinc was introduced into the liquid, to prevent a coating of hydrogen being formed, at the higher temperatures, by the action of the sulphuric acid on the amalgamated zinc. The results obtained with the cells were as follows:—The E.M.F. of a Daniell cell with sulphuric acid increases with the temperature, and the value of the temperature-coefficient depends on the degree of concentration of the liquids in the cell, increasing with an increase in the concentration of the sulphuric acid, until the solution contains about 30 per cent. of the acid, when it attains a maximum value, and diminishes when the concentration is increased beyond this point. The temperature-coefficient increases continuously without attaining a maximum as the concentration of the copper sulphate is increased.

In the case of a zinc sulphate cell, the E.M.F. diminishes as the temperature rises, and when the concentration of the zinc sulphate is increased from a low degree the temperature-coefficient falls to zero, and as the concentration is further increased this has a continually increasing negative value. The effect on the temperature-coefficient of varying the concentration of the copper sulphate solution is the same as in the case of the sulphuric acid cell.

In the accumulator, the temperature-coefficient was found to increase with increased concentration of the sulphuric acid, but the author has not yet been able to determine whether the degree of concentration has any effect on the E.M.F., as the latter begins to diminish as soon as the charging current is discontinued, at first rapidly, and then slowly, but not slowly enough to enable any conclusions to be drawn from the measurements of E.M.F., each of which occupied about six minutes.

During the experiments on the accumulator, whilst evolution of gas was observed from the lead plates when it was placed under the air-pump to free the sulphuric acid from dissolved air, it was found by depositing lead by means of zinc from a solution of lead acetate, and heating it in a vacuum, that finely divided lead absorbs about 0·206 of its volume of hydrogen. The absorption of air by the accumulator plates would be too small to have an appreciable effect on the E.M.F.

The author, however, found it impossible to obtain any trustworthy results from a cell containing platinum instead of copper, owing to the dependence of the E.M.F. on the amount of air absorbed by the platinum. G. W. T.

Determination of the Specific Inductive Capacities of Conducting Liquids. By E. Cohn and L. Arons (*Ann. Phys. Chem.* [2], **33**, 13—31).—In a previous memoir (*ibid.* [2], **28**, 454), the authors gave a means of determining the specific inductive capacity of a conducting liquid founded on the result obtained by them that the dielectric polarisation and conduction are mutually independent. In the former experiments, the highest conductivity did not exceed $4·5 \times 10^{-13}$ in terms of mercury, and the values of the sp. ind. cap. were found to be of much the same magnitude as for good insulators, being in every case less than 5. In the present paper, liquids of higher conductivity are considered, and this made it necessary to devise a new method, as the former one, depending on observations of the rate of leakage of an electrostatic charge, would have required the observations of intervals of time considerably less than the millionth of a second.

The method used for the present inquiry is a modification of Silow's (this Journal, 1876, ii, 267), founded on the principle that when a system of conductors immersed in a homogeneous medium is maintained at a constant potential, the work done against electrical forces, in effecting a given change of configuration, is proportional to the sp. ind. cap. of the medium. The needle and one pair of quadrants of an electrometer were joined to one extremity of the secondary of an induction coil, and the remaining pair to the other extremity. Readings were then taken alternately with the liquid and with air only in the electrometer. By this means measurements could be obtained for liquids having a conductivity as high as 16×10^{-10}, or about 3400 times the highest conductivity in the former series. Calling K the sp. ind. cap., and k the conductivity, it was found that for distilled water $K = 76$, whilst k varied from $3·4 \times 10^{-10}$ to 16×10^{-10}, so that an increase of conductivity to about five times its original value had no perceptible effect on the sp. ind. cap. For ethyl alcohol containing 2 per cent. of water, $K = 26·5$, and when, by the addition of traces of ammonium chloride, the conductivity was increased from $2·3 \times 10^{-10}$ to 12×10^{-10}, the value of K remained sensibly constant. For amyl alcohol the values obtained were $K = 15$ and $k = 0·16 \times 10^{-10}$. When successive quantities of ethyl alcohol were added to pure xylene, both K and k increased, but the latter at first much more rapidly than the former, the change of k from less than 10^{-4} to 0·03 being accompanied only by a change of K from 2·36 to 3·08.

For these substances, Maxwell's law connecting sp. ind. cap.

and index of refraction does not hold even approximately, the deviation from the law being very much greater than even in the case of glass and the fatty oils. The author suggests that it would be of interest to investigate the sp. ind. caps. of aqueous and alcoholic solutions of various salts to as high a degree of concentration as possible, and also to determine the same constant for as many well-defined chemical compounds as possible, in order to see if it may not be possible to find some law connecting the sp. ind. cap. of a substance with its chemical constitution. G. W. T.

Conductivity and Specific Inductive Capacity. By E. Cohn and L. Arons (*Ann. Phys. Chem.* [2], **33**, 31—32).—In this note the authors state that the numbers 2·23 and 4·43 given by them in the paper referred to (*ibid.* [2], **28**, 454) as the specific inductive capacities of xylene and castor oil respectively are, according to their later researches, too small, and should be 2·36 and 4·82 respectively.

G. W. T.

Specific Inductive Capacity of Liquids. By F. Tomaszewski (*Ann. Phys. Chem.* [2], **33**, 33—42).—The principal object of this investigation was to obtain measurements of the specific inductive capacities of certain liquids in order to determine, if possible, some relation between the value of this constant and the chemical constitution of the liquid, which curiously enough was one of the desiderata suggested by Cohn and Arons (preceding Abstracts).

There were two questions which presented themselves for solution: (1) The influence of the number of atoms in a molecule, requiring determinations for isomeric, homologous, and metameric compounds. (2) The effect of introducing a fresh element into the molecule, requiring determinations for non-homologous compounds.

The experiments were carried out by Silow's method slightly modified, and the charges were obtained from a battery of 40 zinc-copper-water cells.

The principal results obtained are given below, K being the specific inductive capacity, and μ the index of refraction for infinite wave-length.

Isomeric Compounds, $C_{10}H_{16}$.

	$\sqrt{K}$.	μ.
Oil of turpentine from *Pinus silvestris*, lævorotatory	1·5070	1·4689
Oil of turpentine from *Pinus maritima*, lævorotatory	1·5026	1·4561
Oil of turpentine from *Pinus Australis*, dextrorotatory	1·5046	1·4685
Oil of citron	1·4990	1·4706

Homologous Compounds. Aromatic Hydrocarbons.

	$\sqrt{K}$.	μ.
Benzene (free from thiophen)	1·4892	1·4757
Toluene	1·5175	1·4713
Paraxylene	1·5436	not determined.
Cumene	1·5627	1·4838

The specific inductive capacities of isomeric compounds are, therefore, not equal.

Where M is the molecular weight and d the density, it was found that the quantity $M(n - 1)/d$, or the molecular refraction, was sensibly constant for the isomeric series, as also were the quantities $M(K - 1)/d$ and $M(\sqrt{K} - 1)/d$. The specific inductive capacity of homologous compounds is seen from the second table to increase with the number of atoms. Maxwell's relation $d = \sqrt{K}$ is only approximately true, as is clear from the tables given. G. W. T.

Electric Discharge through Gases. By A. SCHUSTER (*Proc. Roy. Soc.*, **42**, 371—379).—A glass vessel is divided into two compartments by means of a metal plate nearly reaching to the sides and connected to earth. In one compartment charged gold leaves were placed, in the other electrodes through which discharges were passed from an induction coil. No effect was observed at the atmospheric pressure, but at 43 mm. pressure the leaves slowly collapsed. In another experiment, sparks from a Voss machine were passed at the atmospheric pressure between points or spheres in the neighbourhood of charged balls. When the electrodes were similar, whether points or spheres, the balls collapsed when electrified positively, but when one electrode is a sphere and the other a point, the balls collapse if their electrification is of opposite sign to that of the point. Finally, the author observes that in a partial vacuum incompletely divided into two compartments by a metal screen connected to earth, a continuous discharge between electrodes in one compartment renders it possible to send a current between electrodes in the other compartment with an indefinitely small electromotive force. In one case, a current of 0·008 ampère through the main electrodes enabled an E.M.F. of one-fourth volt to send a current through the auxiliary electrodes. The intensity of the auxiliary current is greater the greater the main discharge and the reduction of pressure; it increases less rapidly than the electromotive force causing it. Anything which facilitates gaseous diffusion increases the strength of the auxiliary current.

In explanation of these facts, the author considers that the two atoms of a gas molecule are charged with opposite electricities, and are held together by molecular forces. When this union is ruptured by the main discharge, the atoms diffuse across to the auxiliary electrodes, and give up their electricities to them. The rupture of the molecule is supposed to take place at the negative pole. The diurnal variations of terrestrial magnetism are supposed to be due to currents produced by tidal or other regular motions, such feeble currents being rendered possible by the more powerful discharges which take place in the upper regions of the atmosphere. H. K. T.

Conduction of Electricity through Gases. By F. NAHR (*Ann. Phys. Chem.* [2], **33**, 295—301).—Hittorf (*Ann. Phys. Chem.*, **7**, 595) found that a pair of gold leaves attached to a stick of shellac, enclosed in a tube of hydrogen containing phosphoric acid to ensure perfect dryness, retained their charge after the lapse of four days, from which he concluded that dry hydrogen does not conduct electricity. Nahrwold (*ibid.*, **5**, 460), by a different method of experimenting, came to the conclusion that the particles of a gas cannot receive an electrostatic charge, and that the loss of charge of a conductor exposed to the air is due entirely to the presence of floating particles of dust. The author considers that Nahrwold's experiments only show that dust is the chief factor in causing leakage in a conductor exposed to the air.

He refers to some former experiments (*ibid.* [2], **5**, 145; **8**, 266; **11**, 155; **16**, 558; **22**, 550) made by him with a charged sphere suspended within an insulated conducting envelope containing different gases of various densities, carefully freed from dust. Whilst he confirmed Hittorf's result as to the charge being retained for a long time, he found that there is an instantaneous small loss of charge, depending on the nature of the gas and on its density. This instantaneous loss increases as the density is diminished, and a further instantaneous loss takes place when the envelope is connected to the earth, followed by a gradual and continuous loss of charge. The author attributes this sudden loss to a transference of electricity to the gaseous molecules, and the slow dispersion to an electrical connection between the sphere and the envelope. He has now repeated the experiments with a double metallic envelope containing gas. The envelopes were in the form of cylinders open at one end, and closed at the other, the closed ends being hemispherical. The open ends were closed by a sheet of glass covered with lac varnish, and the cylinders were cemented to it with their axes coinciding. The author then found a similar increased loss on connecting the outer envelope with the earth, from which he concludes that the gas between the two cylinders acted as a conductor, putting the inner one in connection with the outer, and so with the earth. The instantaneous loss of charge was found to increase when the density of either the inner or the outer portion of gas was diminished, which agreed with the former results, but the slow dispersion of the charge appeared to be sensibly independent of the density of the gas, as would be expected to be the case if the dispersion takes place by a convection of electricity by the gaseous particles, owing to the enormous number in contact with the surface of the envelope at any moment.

G. W. T.

Electrical Conductivity of Solutions of Neutral Salts. By G. JÄGER (*Monatsh.*, **8**, 721—724).—The electrical conductivities of some salts of heavy metals have been measured in solutions containing proportions varying from $\frac{1}{20}$ to $\frac{1}{1280}$ of the gram-molecular weights per litre. The salts thus examined were lead nitrate and acetate; silver nitrate, sulphate, and acetate; zinc sulphate, bromide, and iodide, and copper sulphate and acetate. Dividing the observed conductivity by the proportion of the molecular weight in each case, the relative conductivity of the molecular weight of the salt for different dilutions is obtained. This plotted against the dilution values gives curves approximating to straight lines, although in no case could the conductivity be represented as of the form $L = \alpha m + \beta m^2$. All the curves, with the exception of that for zinc bromide, appear to tend towards maxima in different directions; this is taken as supporting the view that each salt has its own definite molecular conductivity. H. C.

Comparative Properties of the Electrical Conductivities of Salt Solutions. By G. Jäger (*Monatsh.*, **8**, 725—733).—In a former paper (this vol., p. 217), the author proved that if L and L_1 are the molecular conductivities of two different salt solutions, δ the diameter of the molecule of the solvent, and d, d', d_1, d'_1, those of the ions, $\frac{L}{L_1} = \frac{1/(d + \delta)^2 + 1/(d' + \delta)^2}{1/(d_1 + \delta)^2 + 1/(d'_1 + \delta)^2}$. From this it follows that as δ is increased, the value of L/L_1 will more nearly approximate to unity, or that as the size of the molecules of the solvent increase all molecular conductivities approach more nearly to the same value. A rise of temperature increasing the sphere of action of the molecule in accordance with the coefficient of expansion of the liquid, where this last is small and only small changes of temperature are dealt with, δ may be looked on as constant, and the above ratio as independent of temperature.

To test the above, a determination was made of the conductivities of solutions of sodium and potassium chlorides containing $\frac{1}{4}$ to $\frac{1}{32}$ gram-equivalent per litre in water, and in water containing 20 to 60 per cent. alcohol, glycerol, and sugar, in each of which cases the conductivity of the solvent may be neglected. Dividing the molecular conductivity of potassium chloride by that of sodium chloride in each case, it was found, as was expected, that water gave the highest values for the ratio, and that in the other cases the ratio decreased and approximated more to unity as the quantity of dissolved alcohol, glycerol, or sugar increased, or, as may be assumed, the diameter of the molecule of the solvent increased. That temperature would have no effect on the value of the ratio may be taken as proved by the result of Kohlrausch's experiments, "that the resistances of the ions in water are all altered in the same proportion by change of temperature."

Also, as a consequence of Kohlrausch's theory, $L/L_1 = (u + v)/(u_1 + v_1)$ where u, v, u_1, and v_1 are the molecular velocities of the ions, it follows that if two salts have one ion in common, say, $u = u_1$, then L/L_1 approximates to unity as u increases, or the greater the molecular conductivities of two salts containing a common ion, the less will the ratio of the two conductivities differ from unity. This is also found to hold good when tested by the results of Kohlrausch's own experiments. H. C.

The Electrical Conductivity of Solutions of some Fatty Acids in Water and in Alcohols. By K. HARTWIG (*Ann. Phys. Chem.* [2], **33**, 58—80).—The author points out that comparatively few investigations have been made into the conductivity of other than aqueous solutions. Of those known to the author, Mateucci (*Ann. Chim. Phys.*, **66**, 237) was the first who made experiments on alcoholic solutions, but Wiedemann has thrown doubt upon his conclusion that aqueous and alcoholic solutions of the same substance of the same specific weight conduct equally well. Oberbeck (*Ann. Phys. Chem.*, **155**, 595) measured the resistances of aqueous and alcoholic solutions of cadmium bromide and cupric chloride, and found that the conductivity was increased by each of these salts in a manner dependent on the salt and on the solvent. Guglielmo (*Atti R. Accad. Torino*, **17**) determined the conductivity of an alcoholic solution of potassium hydroxide, that of the aqueous solution having been previously determined by F. Kohlrausch. Vincentini (*Mem. R. Accad. Torino* [2], **36**, 22) investigated the conductivity of alcoholic solutions of some chlorides, and found that there is no simple relation between the solubility and the conductivity. Bartoli (*l'Orosi*, **7**, 3) showed that paraffin and naphthalene can be made into conductors by the addition of amylic alcohol and phenol. The same author (*R. Acad. Lincei*, **1**, 550) investigated the conductivity of various mixtures of organic compounds; and Lenz (*Mem. Ac. Sci. St. Pétersbourg*, **7**, 30) made some researches in the conductivity of aqueous and alcoholic solutions, in the course of which he completely demonstrated the falseness of Mateucci's conclusions. The author selected the fatty acids for his experiments, as being very soluble in several media.

The measurements were made by the Wheatstone bridge method, with a telephone as indicator. The substances experimented on were solutions of formic, acetic, and butyric acids in water, and in methyl, ethyl, and amyl alcohols. The measurements were made immediately after the solutions were made, and as none of them occupied more than an hour, it was found that the results were not sensibly affected by the etherification which always takes place when organic acids and alcohols are mixed.

With the exception of two of the solutions of formic acid, the author finds that the conductivity reaches a maximum at a certain concentration, and that this maximum is reached the sooner the worse the conductivity of the acid.

The table below gives the percentage of acid for which each solution has the maximum conductivity:—

Solution.	Acids.		
	Formic acid.	Acetic acid.	Butyric acid.
Water	30	16·6	12·0
Methyl alcohol	100	30·0	17·3
Ethyl alcohol	100	49·0	21·6
Amyl alcohol	—	54·0	26·0

Thus the greater the quantity of carbon present in the acid the sooner is the maximum conductivity attained, and the greater the quantity of carbon present in the solvent the later is the maximum attained, the conductivity being diminished by an increase of the quantity of carbon present either in the acid or in the solvent.

The author attributes the anomalous behaviour of formic acid with regard to electrical conductivity, together with similar anomalies which it exhibits with respect to its other physical properties, to the absence of the group methyl from its composition. G. W. T.

Electric Leakage. By J. J. Thomson and H. F. Newall (*Proc. Roy. Soc.*, **42**, 410—429).—The liquid experimented on is contained in a cylindrical, metallic vessel, connected to earth, in which a metal cylinder is suspended by means of a silk thread; this can be connected either with a battery or with a quadrant electrometer. The inner cylinder, after being charged, is connected with the electrometer, and readings taken every five seconds. Curves are plotted showing (1) the decrease of potential with time; (2) the ratios of successive potential values. The liquids examined were benzene, olive oil, carbon bisulphide and paraffin oil, and were filtered many times before use. With the first three, no deviation from Ohm's law could be detected. With paraffin oil, the conductivity is slightly greater with large than with small differences of potential. These results, where the E.M.F.'s were 20—100 volts, differ from those of Quincke (Abstr., 1886, 959), who finds that with E.M.F.'s sufficient to produce a spark the conduction does not even approximate to Ohm's law. With carbon bisulphide, great discrepancies were found in the first results; these were traced to differences in time of charging, and later experiments proved that electric absorption took place. The effect was greatest after redistilling the carbon bisulphide, but at times it was totally absent. The conductivity of all the liquids was increased by rise of temperature, so that in this respect they resemble electrolytes. H. K. T.

The Influence of Magnetic Forces on the Nature of the Heat Conductivity of Bismuth. By A. v. Ettingshausen (*Ann. Phys. Chem.* [2], **33**, 129—136).—The author points out that Righi (Abstr., 1887, 1009) and Leduc (*Compt. rend.*, **104**, 1783; **105**, 250) have made some experiments, from which they conclude that the thermal conductivity of bismuth in a magnetic field is diminished to an equal extent with the electrical conductivity, supposing the magnetic lines of force to cut the stream lines for heat or electricity respectively at right angles. Nernst (*Ann. Phys. Chem.* [2], **31**, 760) was unable to detect any change in the thermal conductivity. The author, after some experiments made with great care, finds that the thermal conductivity is diminished, but to a much less degree than the electrical conductivity. The decrease in the thermal conductivity is greater when the bismuth is impure, but still much less than that of the electrical conductivity. G. W. T.

Constancy of the Heat Produced by the Reaction of Silver Nitrate with Solutions of Metallic Chlorides. By T. W.

RICHARDS (*Chem. News*, **57**, 16—17).—In these experiments, all necessary precautions are observed to obtain comparable conditions: 250 c.c. of the silver nitrate solution (equal to 4 grams silver nitrate) and 250 c.c. of the salt solution (containing a gram or so of the salt in excess of that required to precipitate all the silver) are poured simultaneously into the platinum calorimeter (Berthelot's), and the rise in temperature noted. The average rise in 20 experiments amounts to 16·165 cal. and all the results are practically identical; the experiments included sodium, potassium, ammonium, barium, cupric, zinc, manganous, nickelous, ferrous, aluminic, ferric, and chromic chlorides and hydrochloric acid. Taking the following equation as representing the reaction, the author concludes from these results that the amount of heat is constant no matter what R m or n may be. $\left(\frac{1}{n}R_mCl_n + AgNO_3 + Aq\right) = AgCl + [\frac{1}{2}R_m(NO_3)_n = Aq]$. (Compare Pickering, this vol. p. 333.) D. A. L.

Relation between the Heats of Formation of Chlorides and Sulphates in Aqueous Solution. By I. W. FAY (*Chem. News*, **57**, 36—37).—The author conducted a series of experiments with barium chloride and soluble sulphates exactly similar to Richard's experiments with silver nitrate and chlorides (see preceding Abstract). There is not that general regularity observed in the case of the sulphates as with the nitrates, although the rise for allied bases is quite close; the sesquioxide salts give a greater rise of temperature than the protoxide salts do, and with the double salts a still larger quantity of heat is evolved, whilst sulphuric acid gives most of all. The sulphates included in the experiments were sodium, potassium, ammonium, magnesium, zinc, cadmium, copper, nickel, cobalt, ferrous and ferric, and aluminium potassium alum, potassium chrome-alum, ammonium ferrous sulphate, and sulphuric acid. The results are tabulated in the original paper. (Compare Pickering, this vol., p. 333.) D. A. L.

Alteration in the Volumes and Density of Liquids by the Absorption of Gases. By K. ÅNGSTRÖM (*Ann. Phys. Chem.* [2], **33**, 223—233).—The author has already given an account of investigations on expansion of water through the absorption of gases (Abstr., 1882, 687). Since this appeared, experiments of the same nature have been made both for water and ethyl alcohol, by Blümcke (Abstr., 1885, 215; 1887, 435), but they do not agree with those made by the author or by Mackenzie and Nichols (Abstr., 1878, 366) and Nichols and Wheeler (*Phil. Mag.*, **5**, 11, 113), probably because Blümcke's method did not allow of several requisite corrections being made; for example, for the compression of the areometer, and for the refraction of light at the surface of the containing vessel.

A summary of the results of the author's previous experiments and of the first series described in the present paper are given in the table below, in which δ_1, δ_2, δ_3, are coefficients of expansion due to absorption.

	Carbonic acid δ_1.	Air δ_2.	Hydrogen δ_3.	$\frac{\delta_1}{\delta_3}$.	$\frac{\delta_2}{\delta_3}$.
Chloroform	0·00188	0·00205	0·00160	1·18	1·28
Nitrobenzene	0·00168	—	—	—	—
Water	0·00130	0·00143	0·00106	1·23	1·35
Benzene	0·00200	0·00216	0·00170	1·18	1·27
Methyl alcohol	0·00184	0·00201	0·00157	1·17	1·28
Ethyl alcohol	0·00185	0·00203	0·00152	1·22	1·34
Ether	0·00200	0·00240	0·00184	(1·09)	1·30
			Means =	1·20	1·30

This shows that, except for ether, the ratios δ_1/δ_3 and δ_2/δ_3 are sensibly constant. Experiments on the successive absorption of two or more gases gave the result that the coefficient of expansion due to absorption is independent of any previous absorption of gas, the total expansion being equal to the sum of the expansions due to the absorption of the different gases.

The results obtained enable the change in the specific weight of a liquid due to the absorption of gas to be calculated, which is of practical importance for specific weight determinations, but the effect in such cases is so small that it need only be taken into account when the most extreme accuracy is desired. The author considers the constancy of the ratios δ_1/δ_3 and δ_2/δ_3 to be the most important of his results from a theoretical point of view, as it shows that the dilatation depends on the gas, and that the relations between the coefficients of dilatation due to absorption are independent of the nature of the liquid; from this he concludes that Ostwald's hypothesis (*Stöchiometrie*, p. 356), founded on the values of the coefficient of dilatation due to absorption obtained by the author and by Sarrau, namely, that "the volume of the absorbed gas is almost exactly reduced to the volume of its molecules," is *à priori* extremely improbable. G. W. T.

Differential Tonometer. By G. J. W. Bremer (*Rec. Trav. Chim.*, 6, 122—136).—An apparatus for measuring the difference between the vapour-tension of a saline solution and the vapour-tension of water by allowing the vapours to act on the opposite ends of a column of olive oil. It consists essentially of small flasks connected with vertical tubes about 150 mm. high communicating with one another by means of a horizontal tube at the bottom. The particular apparatus described consists of four such flasks. The flasks should have exactly the same cubical contents, which may be adjusted by introducing pieces of glass rod, and should contain equal volumes of the solutions. After introduction of the liquids the flasks are cooled to 0°, rendered partially vacuous, and oil allowed to enter from the bottom horizontal tube until it rises to about half the height of the vertical tube. The exact pressure of the air in the flasks is observed, and the flasks and their contents are heated to different temperatures and the differences between the levels of the oil in the tubes are observed.

Determinations of the vapour-tensions of aqueous solutions of calcium chloride of different strengths show that if the salt is regarded as existing in the liquid in the anhydrous condition, the reduction of the vapour-tension increases more rapidly than the amount of calcium chloride present, but if the solution is supposed to contain the hydrate $CaCl_2 + 6H_2O$, the reduction of the vapour-tension is proportional to the amount of salt present, as Wullner has previously stated. C. H. B.

Dynamical Method of Determining Vapour-pressure. By G. Tammann (*Ann. Phys. Chem.* [2], **33**, 322—337).—The author on recalculating some tables given by Regnault (*Ann. Chim. Phys.* [3], **15**, 158) for the vapour-pressure of pure water determined by the dynamical and statical methods respectively, found that the close agreement of the results was only apparent, and that there were really some considerabe discrepancies which could not be accounted for. The author now describes a number of experiments carried out principally with a view to testing the dynamical method, following Regnault with some modifications in details. He concludes that the method is not capable of giving good results. In the case of unsaturated solutions, when the current of air is passed over the surface of the solution, the upper layers become more concentrated than the lower, through the evaporation being entirely superficial, and if the current of air is led through the solution errors are introduced, as it is impossible to prevent variation of pressure and the scattering of drops of the solution upon the interior of the glass vessels. The author attempted to use it with saturated solutions, using filter-paper soaked in the solution, then partly dried, and introduced into a U-tube through which the current of dry air was allowed to pass, but then he was met by the difficulty that on taking the tube out of the bath used to maintain the required temperature, drops of water condensed on the inner surface of the tube, and dissolving some of the salt adhering to it gave rise to unsaturated solutions. The author next tried the method with hydrated salts in crystals. Here, however, the results were found to depend on the velocity of the stream of air, which appeared to be due to the water-vapour given off dissolving a portion of the crystals and forming hydrates containing less water, which would give a lower vapour-pressure.

From some of the results obtained during the last series of experiments, combined with Pape's result (*Ann. Phys. Chem.*, **124**, 329) that rates of evaporation from the different surfaces of irregular crystals are not the same, the author draws the conclusion that the vapour-pressure at the surface of a crystal is not the maximum value of vapour-pressure due to the crystal. The vapour-pressure at the surface depends on the nature of the surface, and is considerably less when the surface is uninjured than when it is broken or otherwise changed. G. W. T.

Compressibility of Rock Salt. By F. BRAUN (*Ann. Phys. Chem.* [2], **33**, 239—240).—The author in a recent note (this vol., p. 214), whilst giving the preference to Röntgen and Schneider's value 5×10^{-6} for the cubic compressibility of rock salt over the value $1·4 \times 10^{-6}$ found by him, as his own determination was a comparatively rough one, pointed out that according to Voigt's measurements of elasticity the value would be $1·6 \times 10^{-6}$. The author has since seen a later paper by Voigt (*Ann. Phys. Chem.* [2], **15**, 497) in which he corrects his former result, as in obtaining it he made use of a torsion formula which he has since found to be incorrect. Voigt's later measurements would give the value $4·2 \times 10^{-6}$, which, considering the difficulty of the piëzometer method, agrees fairly with that obtained by Röntgen and Schneider. G. W. T.

Rate of Transformation of Metaphosphoric Acid. By P. SABATIER (*Compt. rend.*, **106**, 63—66).—The conversion of metaphosphoric acid into orthophosphoric acid involves the introduction of an acid function of medium activity and an acid function of feeble activity, in addition to the original energetic function. Only the latter affects methyl-orange; the second feebler function affects phenolphthaleïn, the third can only be qualitatively recognized by means of the blue C4B. The acidity of the liquid h to methyl-orange remains constant, whilst its acidity to phenolphthaleïn ϕ increases, and affords a measure of the progress of the transformation. When conversion into orthophosphoric acid is complete $\phi = 2h$, and at any stage of the change $2h - \phi$ gives the amount of metaphosphoric acid y still remaining unaltered.

The metaphosphoric acid was obtained by dissolving phosphoric anhydride gradually in cold water, and also by strongly heating the ortho-acid, and dissolving the residue in water. Both preparations behaved in the same manner.

These solutions were heated at different temperatures for definite intervals of time. At a given temperature, log y is proportional to the time. The velocity of the change at each instant is proportional to the mass of transformable substance present in the system, and hence $\log y = -x \log a + \log b$, and therefore $y = ba^{-x}$, where b is the value of y at the commencement, and a is a constant which is a function of the temperature and the concentration, and increases with both, but the exact law of increase has still to be determined.

C. H. B.

Point of Transition and Point of Fusion. By J. H. VAN'T HOFF (*Rec. Trav. Chem.*, **6**, 36—42; 91—94; 137—139).—The particular reaction considered is the conversion of mixtures of sodium and magnesium sulphates into astrakanite, $Na_2Mg(SO_4)_2 + 4H_2O$, at temperatures below 21·6°. It is found that in order to separate sodium sulphate from the mother-liquors from sea-water, which contain a large proportion of magnesium chloride, it is necessary to cool the liquid below 5°, and hence it would appear that the system $MgCl_2 + Na_2SO_4$ is stable below 5°, but at higher temperatures the reciprocal system is formed.

If a solution containing sodium sulphate and magnesium chloride in equivalent proportions is placed in a dilatometer, no anomalous expansion is observed at 5°, but if 2 mols. of sodium sulphate are present for each molecule of the magnesium salt, there is a very considerable expansion if the liquid is heated above 5°, and a considerable contraction if it is cooled below this temperature. This particular temperature is in fact the point of transition between the two systems, but the author has previously observed that magnesium chloride cannot exist in presence of sodium sulphate at temperatures below 5°, because the tension of the water of crystallisation of the latter salt is less than the vapour-tension of the saturated solution of the two salts.

The slow evaporation at a low temperature of a solution containing sodium chloride and sodium and magnesium sulphates in equivalent proportions yields a mixture of the three salts, but if evaporation takes place at a higher temperature cubical crystals of sodium chloride are obtained, together with rosettes of astrakanite, which is formed by the union of the two sulphates with elimination of water. In presence of sodium chloride, formation of astrakanite takes place at 6°, and the reverse change at lower temperatures, whilst in absence of sodium chloride astrakanite is formed at 21·6° (Abstr., 1886, 968). The reduction of the point of transition from 21·6° to 5° by the presence of sodium chloride, corresponds with the reduction which this salt produces in the freezing point of its solution.

The double acetate, $CuCa(C_2H_3O_2)_4 + 8H_2O$, decomposes at 75° into the simple salts $Ca(C_2H_3O_2)_2 + H_2O$ and $Cu(C_2H_3O_2)_2 + H_2O$, with elimination of 6 mols. H_2O, and the change is accompanied by a distinct contraction; at lower temperatures, the double salt is formed, and expansion takes place. The volume changes are analogous to those which accompany the solidification of water, and it was to be expected that the effect of pressure would be analogous in the two cases.

At the author's request, Spring has subjected the double acetate to high pressures at varying temperatures, and finds that under a pressure of 6000 atmospheres decomposition takes place at 40°. Under the same pressure at 16°, there is no appreciable decomposition if the duration of the experiment is short, but if pressure is prolonged, evidence of decomposition is readily recognisable. Under a pressure of 2000 atmospheres, decomposition takes place distinctly at 50° (compare this vol., p. 341).

Van't Hoff points out that determinations of the minimum pressure required to produce reactions of this kind, together with measurements of the resulting changes in volume, will make it possible to express in kilogram-metres the absorption of energy involved in the reaction, and conversely the liberation of energy resulting from the reverse change. C. H. B.

The Position of Atoms in Space. By J. WISLICENUS (*Ber.*, **21**, 581—585).—Lössen has challenged Van't Hoff and Wislicenus to state their views on units of affinity from the standpoint of their geometric theory, and he affirms that the question of the position of the units of affinity in space must be answered not after, but before, the question of the positions of atoms in space, and above all that a definition of "unit of affinity" must be given (this vol., p. 218).

The author admits that his views quite bar the conclusion that atoms are material points, and it is impossible, therefore, to consider them as configurations in space in which the several chemical units of action of polyvalent elements can be localised. But this conclusion is admissible when the so-called atoms are considered, not as atoms in the strict sense of the word, but as simple groups of primitive atoms, similar to the compound radicles but less complex; and therefore the position of the elementary atoms in the molecule must be determined before Lössen's demand can be taken into earnest consideration.

The author has shown that the determination of the arrangement in space of the atoms in a molecule is within the domain of experiment, and he points out that the study of the configuration of the molecule is the only way to solve successfully the question of the distribution in space of its spheres of action—the so-called units of affinity. Only by studying the properties of molecules can inductive conclusions be drawn as to the properties of atoms.

The author's views are stated as follows:—It is more probable that the atoms are configurations in space composed of atoms of primitive elements than that they are simply points of energy; the most likely assumption is, therefore, that the atoms are comparable with the compound radicles, and, as in the latter, their units of affinity are located in certain parts from which they exercise their action.

It is possible, in time, to succeed in obtaining definite ideas not only of the form of elementary atoms, but also of the relative positions of their spheres of action.

It is not impossible that the atom of carbon resembles more or less in form a regular tetrahedron, and that the causes of those actions, which are evidenced by the units of affinity, are concentrated in the angles of this tetrahedric configuration, perhaps for analogous reasons, and similarly to the electric action of a charged metallic tetrahedron. The real carriers of energy would finally be the primitive atoms, exactly as the chemical energy of compound radicles is the resultant of the energy of the elementary atoms. F. S. K.

The Atomic Weights of the Elements. By A. BAZAROFF (*J. Russ. Chem. Soc.*, 1887, 61—73).—The author finds that the variation in the numbers expressing the atomic weights of the elements, arranged according to the periodic system, is analogous to the changes in the properties of the elements and their compounds. When the most probable numbers for the atomic weights of the elements are arranged according to the periodic law, and, either in the horizontal or in the vertical series, the atomic weight of an element is divided by the atomic weight of the element with the next lower atomic weight, products are obtained which decrease regularly with increase in the atomic weights compared. In the horizontal series, the maximum is found to correspond with the relation of $\frac{\text{Be}}{\text{Li}} = \frac{9{\cdot}08}{7{\cdot}01} = 1{\cdot}2953$, the minimum to $\frac{\text{Bi}}{\text{Pb}} = \frac{207{\cdot}5}{206{\cdot}39} = 1{\cdot}0054$. This decrease, however, is not continuous, the products alternately decreasing and increasing, as is seen from the following examples :—

$$\frac{\mathrm{Mg}}{\mathrm{Na}} = 1\cdot0411,\ \frac{\mathrm{Al}}{\mathrm{Mg}} = 1\cdot1295,\ \frac{\mathrm{Si}}{\mathrm{Al}} = 1\cdot0355,\ \frac{\mathrm{P}}{\mathrm{Si}} = 1\cdot1057,$$

$$\frac{\mathrm{S}}{\mathrm{P}} = 1\cdot0329,\ \frac{\mathrm{Cl}}{\mathrm{S}} = 1\cdot1060, \text{\&c.}$$

This relation is best represented graphically, the order of atomic weights standing as abscissæ, and the aforesaid quotients as ordinates: in this way a curve of zigzag form is obtained. This relation is expressed by the author in the form of a law, namely, that "the increase in the atomic weights of the elements proceeds with a variable intensity, the smaller coefficient of change varying with the larger in such a way that both regularly decrease."

Another regularity is observed in the vertical groups, for example, with the coefficients in the second group :—

$$\frac{\mathrm{Mg}}{\mathrm{Be}} = 2\cdot6366,\ \frac{\mathrm{Ca}}{\mathrm{Mg}} = 1\cdot6671,\ \frac{\mathrm{Zn}}{\mathrm{Ca}} = 1\cdot6257,\ \frac{\mathrm{Sr}}{\mathrm{Zn}} = 1\cdot3456,$$

$$\frac{\mathrm{Cd}}{\mathrm{Sr}} = 1\cdot2795,\ \frac{\mathrm{Ba}}{\mathrm{Cd}} = 1\cdot2252.$$

This change the author expresses by the law: "In the vertical series in the periodic system, the relation of two neighbouring atomic weights decreases with increasing atomic weight, but this decrease is alternately larger and smaller." Neither of these functions extends to the whole periodic system, as there are many elements whose atomic weights are not yet determined with sufficient accuracy. Yet it is possible, from the data which are to hand, to state the following general law: "The magnitude of the atomic weight of each element is determined by the magnitude of the atomic weights of the elements next to it in the periodic system both horizontally and vertically."

The author further analyses the exceptions to the said rules, and expresses the opinion that several of them are due to the atomic weights not being determined with sufficient accuracy, but it is difficult to say how far he is right in correcting several of the better determined numbers (he assumes for Tl 202 instead of 203·7!). Notwithstanding the apparently complicated character of the relation pointed out, the author thinks it possible that when the fundamental data are more exactly determined, it may be possible to calculate the atomic weight of an element with greater accuracy than is the case at present.

B. B.

Raoult's Method of Determining Molecular Weights.* By V. Meyer (*Ber.*, **21**, 536—539). In investigating some derivatives of benzil, two series of isomeric compounds were obtained; both series have the same constitution, in the ordinary sense of the word, and are yet distinct from one another and yield different derivatives. The isomerism of the two series is expressed by the formulæ

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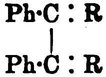
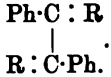
* Raoult's papers on this method are Abstr., 1883, 7, 278, 952; 1884, 254, 701, 808, 952, 1248; 1885, 122, 858; 1886, 197, 763. Compare also this vol., p. 361.



$$\begin{array}{c}\mathrm{Ph{\cdot}C:R}\\ |\\ \mathrm{Ph{\cdot}C:R}\end{array}$$

and



$$\begin{array}{c}\mathrm{Ph{\cdot}C:R}\\ |\\ \mathrm{R:C{\cdot}Ph}\end{array}.$$

By means of a modification of Raoult's method for determining molecular weight by measuring the amount by which the solidifying point of a solvent is lowered by a known weight of a dissolved substance, it is shown that the molecular weight of the compounds of the two series in question is identical. The method employed, which only involves the use of an ordinary thermometer divided into 0·1° and a simple apparatus, will be described. N. H. M.

Application in Chemical Laboratories of Raoult's Method for Determining Molecular Weights. By K. Auwers (*Ber.*, **21**, 701—719).—The use of Raoult's method for determining molecular weights by V. Meyer (preceding Abstract) led to a consideration of the conditions necessary for its successful application. The exception which many solutions, notably those of inorganic salts in water, show to the law put forward by Raoult (Abstr., 1886, 763), renders this law useless for practical purposes, and the relation $M = T/A$, where M is the molecular weight, T the molecular depression, and A the depression caused by 1 gram of substance in 100 grams of solution, is used. It is recommended to first determine the value of T, which will be constant for the series of compounds under consideration, by taking members of the series of known molecular weight. A measurement of A then suffices to determine M in subsequent cases.

A great objection is the impossibility of working with relatively small amounts of material, for although the above relation does not hold for concentrated solutions, the solutions must not be too dilute, and some discrimination is necessary in adjusting the strength to give the depression which should be measured in each case. With regard to the solvents used, it is of course a condition that no chemical action should take place between the one selected and the substance under examination. The selection of a suitable solvent is a matter of great importance.

Water is generally objectionable on account of its tendency to form hydrates and its non-solvent action on most organic compounds. As it is necessary also, according to Raoult, that the depression measured should not be less than 0·5°, as the relation does not hold when it is allowed to sink below that value, a relatively large quantity of material is necessary for each determination. Benzene gives better results, but cannot be used in the case of alcohols, phenols, or acids, and introduces an element of uncertainty in dealing with substances allied to these.

By far the best solvent, and the one that can be used with the greatest range of substances, is glacial acetic acid. The errors in this case are small, and the measurement of a depression of about 0·3° suffices. A great advantage also is that this solvent admits of working at ordinary temperatures. It is, however, found necessary, owing to its hygroscopic nature, to conduct the experiments in a closed space, and an apparatus has been devised and is described by means of which this is easily rendered possible. A thermometer divided to one-tenth of a degree was used, and this was found to give sufficiently accurate results. Experiments are detailed with naphthalene and picric acid, acetanilide and benzil, and the isomeric diacetyl-compounds of β-diphenylglyoxime.

In conclusion, the author recommends the use of Raoult's method in those cases where vapour-density determinations are not possible.

H. C.

Isonitroso-compounds. By E. BECKMANN (*Ber.*, **21**, 766—769). —The application to the ketoximes of Raoult's method for the determination of the molecular weight by the lowering of the freezing point, has led to the important result that the molecular weights are twice as large as has hitherto been assumed. The compounds experimented with were acetoxime and camphoroxime; the solvent being benzene.

With benzaldoxime and anisaldoxime, results were obtained pointing to molecular weights about one and a half times as great as those previously adopted; these results are, however, doubtless due to partial dissociation of the double molecule. A. J. G.

Desiccation of Gases. By J. D. VAN DER PLAATS (*Rec. Trav. Chim.*, **6**, 45—59).—An extended historical summary of the various methods which have been proposed for the desiccation of gases, together with an account of experiments made by the author. Anhydrous calcium chloride is more efficient than calcium chloride containing 2 mols. H_2O, but the difference diminishes at low temperatures. Calcium oxide absorbs moisture more slowly than anhydrous calcium chloride, and leaves twice as much water in the air as calcium chloride containing 2 mols. H_2O. Fused potash acts rapidly and much more completely than anhydrous calcium chloride, but less rapidly and less completely than concentrated sulphuric acid. Potash solution of sp. gr. 1·25 loses a considerable quantity of water if a current of air is passed through it for some time.

Ammonia is almost completely dried by fused potash.

Calcium chloride is a convenient but not very efficient desiccating agent. If the solution has been evaporated at 180°, it always contains calcium oxide, which cannot be neutralised even by the prolonged action of carbonic anhydride or hydrogen chloride so long as the salt remains dry.

Phosphoric anhydride is the best of all desiccating agents at present known, but it is inconveniently light and bulky. Not unfrequently it contains phosphorous anhydride, but this can be removed by Stas's method of distilling it in dry air.

Concentrated sulphuric acid is cheap and convenient, allows the speed of the gaseous current to be watched, and dries gases almost perfectly. It gives off no vapours, and when cooled its efficiency is increased. It must not contain sulphuric anhydride, and the presence of 6 to 8 per cent. of water is desirable in order to ensure absence of the anhydride in the gas which is passed through the acid. Sometimes the acid contains sulphurous anhydride, but this is readily removed by a current of dry air or by boiling the acid. Sulphuric acid will dissolve carbonic anhydride, but this gas is removed in a few minutes by passing a current of air into the liquid. The distribution of sulphuric acid with a view to expose a large surface is best effected by means of broken glass. Pumice should be boiled with sulphuric acid containing a little nitric acid in order to remove chlorides and fluorides and metallic oxides which might absorb oxygen. Sulphuric acid, especially if cooled, is practically as efficient as phosphoric anhydride, and the errors due to its employment are certainly not greater than those arising from the use of india-rubber connections or from neglect to remove, by heating, the layer of moist gas condensed on the surfaces of the glass vessels.

India-rubber cannot be completely dried on a sand-bath, but should be kept over sulphuric acid in the dark for a long time. Tubing with walls 5 mm. thick allows air and aqueous vapour to pass extremely slowly, and its power of absorbing carbonic anhydride is at a minimum.

Drying tubes, &c., which have to be weighed should be kept under a bell-jar containing vessels filled with the same desiccating agent as the tubes themselves contain. C. H. B.

Delicate Thermometer for Lecture Purposes. By S. Young (*Chem. News*, **56**, 261).—For this purpose the author recommends an air thermometer of the form commonly employed to show the expansion of air with rise of temperature, but using a volatile liquid such as ether in place of mercury or sulphuric acid; to make the column of liquid visible at a distance, a little absolute alcohol coloured with aniline red is added. The apparatus employed by the author had the following dimensions: the cylinder at the bottom containing the air confined by ether was 17 mm. in diameter and 130 mm. long, the narrow tube extended 700 mm. above this cylinder and had a diameter of 2·8 mm., above this there was a reservoir large enough to hold the ether when the temperature got beyond the range of the thermometer. The total rise of column for 10° in the thermometer described was 510 mm.; for 1° between 0° and 1° the rise = 40 mm., whilst between 9° and 10° it = 82 mm. D. A. L.

Lecture Experiment for Demonstrating the Valency of Metals. By B. Lepsius (*Ber.*, **21**, 556—561).—The method which Nilson and Petterson have recently described for determining the atomic weights of the rare earths can be employed for demonstrating the valency of metals. A quantity of the pure metal, proportional to its atomic weight, is heated in gaseous hydrogen chloride, the volume of liberated hydrogen being proportional to the valency of the metal. For various reasons many of the metals offer great difficulties in carrying out this experiment, and the author recommends thallium, zinc, and aluminium as the most suitable examples. The hydrogen chloride, which must be perfectly dry, is obtained by acting on solid sublimed ammonium chloride with concentrated sulphuric acid in a Norblad's apparatus; it is passed through a combustion tube which contains weighed portions of the above-named metals (twice the atomic weight) placed at intervals of 10 cm. from one another. The liberated hydrogen is collected in a graduated three-limbed glass apparatus filled with a 5 per cent. solution of potash and provided with a mercury seal. By heating the metals successively, the hydrogen evolved from each can be collected separately and the volumes compared directly. F. S. K.

Inorganic Chemistry.

The Composition of Water by Volume. By A. Scott (*Proc. Roy. Soc.*, **42**, 396—400).—The ratio by volume in which oxygen and hydrogen combine at 0° and 760 mm. is redetermined. The apparatus is so arranged that both gases are measured in the same vessel, a separate vessel being used for exploding. After explosion, the residue was analysed by exploding with oxygen or hydrogen and the impurity (nitrogen and carbonic anhydride) determined. The oxygen was obtained from potassic chlorate and from mercuric oxide prepared from the nitrate, the hydrogen was obtained by electrolysis. The ratio obtained is 1·994 : 1, which with 15·9627 for the density of oxygen, gives 16·01 as the atomic weight of oxygen. H. K. T.

The Weldon-Pechiney Process for the Manufacture of Chlorine from Magnesium Chloride. By J. Dewar (*J. Soc. Chem. Ind.*, **6**, 775—790).—This process, which was patented in June, 1884 (Eng. Pat. 9306), has recently been worked at Salindres on an experimental plant designed for the daily production of 1 ton of chlorine, and may be briefly described as follows:—The raw material employed is hydrochloric acid, the operations being (1) dissolving magnesium oxide in hydrochloric acid; (2) preparing magnesium oxychloride; (3) crushing, breaking, and sifting the oxychloride; (4) drying the oxychloride; and (5) decomposing the oxychloride. The magnesium oxide to be dissolved in hydrochloric acid is a portion of that which results from the fifth operation. The hydrochloric acid also results in part from the fifth operation and the remainder from the decomposition of salt. The solution obtained is evaporated down to the point at which it will contain not more than about six equivalents of water, and is then converted into oxychloride by mixing one equivalent of magnesium chloride with one and a third equivalents of magnesium oxide. This operation lasts only about 20 minutes, but during this time the whole mass becomes very hard and during solidification disengages much heat. The product is then in the form of solid pieces of different sizes along with a small quantity of powder. It is necessary to reduce this material to fragments, of which the largest shall not exceed the size of a walnut, and further to clear them of dust which might, when in the decomposing furnace, prevent free passage of air through the mass; this is effected by crushing it between cylinders bristling with diamond points, and then passing it through a rotating sieve. The oxychloride is then dried, this operation being necessary, as in the decomposition a larger quantity of free chlorine and a smaller amount of hydrogen chloride are produced if the material contains less water, and the decomposition is performed at a higher temperature, both conditions being realised by drying previous to decomposition. The dried oxychloride is then decomposed in a special apparatus consisting of a series of furnaces provided with decomposing chambers heated by a movable regenerative burner, the oxychloride being decomposed in a current of air. The author's theory of the decomposition which goes on in the furnace is that in the first stage there is a rapid evolution of steam, the steam decomposing a portion of the magnesium chloride with formation of hydrogen chloride which passes off with the vapour of water. Anhydrous magnesium chloride and magnesium oxide remain, and this mixture then undergoes decomposition into magnesium oxide and chlorine by the action on it of atmospheric oxygen. The products are drawn off from the furnace by means of a diminished pressure steadily maintained, an aspirator being employed which acts through an ordinary hydrochloric acid condensing tower, a number of sandstone bonbonnes and a glass tube refrigerator, the latter being in immediate connection with the decomposing furnace. The hydrochloric acid is condensed in these apparatus, whilst the mixture of air and chlorine passes on through the aspirator and is employed for the manufacture of chlorate: for this purpose, it is driven into special apparatus, wherein the chlorine acts on calcium hydroxide and gradually transforms it into a mixture of calcium chlorate and calcium chloride. D. B.

Nitrogen Chloride. By L. Gattermann (*Ber.*, **21**, 751—757).—The composition of nitrogen chloride has not yet been satisfactorily determined; weighed quantities of the chloride have never been analysed, but merely the ratio of nitrogen to chlorine determined in an unknown amount of the chloride, and, as is well known, the results obtained by different observers are by no means in accordance. In the present research, the experiments were carried on as far as possible in the glass case devised by V. Meyer (*Ber.*, **21**, 26).

The nitrogen chloride was prepared in the usual manner by the action of chlorine on a solution of ammonium chloride. No sign of the formation of the chloride was visible until more than half the chlorine was absorbed, when the formation of minute drops was noticeable in the layer of liquid drawn up by capillary attraction on the sides of the flask; this soon spread and formed a thin film on the surface of the liquid, and this film in turn gradually separated into larger drops, the heavier of which sank, but were again brought to the surface by the nitrogen bubbles formed in the slight decomposition which goes on. When no more drops are formed, the chloride by careful shaking was made to fall into a small leaden capsule provided with a handle. It was then poured, with the aid of a funnel, into a thin-walled separating funnel, the ammonium chloride solution removed by a pipette, and the nitrogen chloride repeatedly washed by shaking with water until the washings no longer gave a chlorine reaction. To assist the removal of dissolved chlorine from the oil, air was repeatedly blown through it by means of a glass tube, so that the oil was disseminated through the liquid in small drops. The successful carrying out of these operations shows that nitrogen chloride is by no means so readily exploded as has usually been supposed. The purified oil was next transferred to a thin glass flask (an operation attended with much danger owing to the friction of the stopcock of the separating funnel), dried by agitation with a small, clean piece of fused calcium chloride, and poured into the weighing glass—a weighed cylindrical vessel of about 1 c.c. capacity, provided with a stopper not quite air-tight. The weighing was effected in the usual manner, save that a glass screen was again employed. The weighed substance was then decomposed by aqueous ammonia, and the chlorine estimated as silver chloride. The results showed that the product of the action of chlorine on ammonium chloride is invariably a mixture of several chlorinated ammonias, and that the product was richer in chlorine the longer the oil was in contact with chlorine, but under no conditions was the trichloride obtained directly.

After washing out the ammonium chloride as described above, the separating funnel containing the crude product covered with a few drops of water was placed horizontally, and a moderately strong stream of chlorine passed through for half an hour. The oil so obtained, after washing and drying, was analysed, and proved to be pure nitrogen trichloride.

Nitrogen chloride explodes on exposure to a strong light—either bright sunshine or magnesium light, although not so readily in the latter case. As in the author's experiments, no explosions occurred for which a cause could not be assigned, it seems very probable that the so-called spontaneous explosions experienced by other observers may be attributed to the action of light.

About $\frac{1}{2}$ gram of nitrogen chloride was heated in a thin-walled tube immersed in a beaker filled with liquid vaselin. Up to 90° no change was observed, but about 95° a violent explosion suddenly occurred. As has been noticed before in the explosion of nitrogen chloride, the main force of the explosion was exerted in a downward direction.

A. J. G.

Pyrophosphates. By G. v. KNORRE and E. OPPELT (*Ber.*, **21**, 769—773).—Pahl has stated (this Journal, 1875, 375, 774) that he obtained an acid calcium pyrophosphate by the action of oxalic acid on normal calcium pyrophosphate: although closely following his directions, the authors have failed to obtain any such salt, pyrophosphoric acid being formed, nor is any acid pyrophosphate formed by the action of pyrophosphoric acid on the normal salt.

By adding calcium chloride to a moderately concentrated solution of dihydrogen disodium pyrophosphate, a white, crystalline precipitate is obtained of the formula $2CaH_2P_2O_7,Ca_2P_2O_7 + 6H_2O$, this can be recrystallised from hot water in which it is very sparingly soluble. When this is boiled for a long time with hot water, it is decomposed, and the residue, after thorough washing, has the composition

$$CaH_2P_2O_7,Ca_2P_2O_7 + 3H_2O.$$

From concentrated solutions of strontium chloride and dihydrogen sodium pyrophosphate, a slight flocculent precipitate of the composition $2Sr_2P_2O_7,H_2SrP_2O_7 + 6H_2O$ is obtained; from dilute solutions, a crystalline precipitate separates of the formula $3Sr_2P_2O_7,SrH_2P_2O_7 + 2H_2O$, whilst if the solution is heated to boiling, the salt

$$3Sr_2P_2O_7,SrH_2P_2O_7 + H_2O$$

is formed.

Solutions of barium chloride and dihydrogen sodium pyrophosphate when mixed in the cold yield the white crystalline salt

$$Ba_2P_2O_7,BaH_2P_2O_7 + 3H_2O.$$

A. J. G.

Action of Arsenious Trisulphide on Iodine. By R. SCHNEIDER (*J. pr. Chem.* [2], **36**, 498—515).—A solution of iodine in carbon bisulphide is without action on natural arsenious trisulphide (orpiment), but reacts with that precipitated by hydrogen sulphide, forming arsenious iodide and sulphur. Attempts to prepare the compound $As_2S_3,2AsI_3$ by heating a mixture of iodine and arsenious trisulphide in the ratio $As_2S_3 : 6I$, were not successful. The mixture fused at a low temperature to a homogeneous mass of a brown colour, which dissolved almost entirely in carbon bisulphide; on evaporation of the solvent nothing but arsenious iodide and sulphur crystallised out. On distilling a mixture of arsenious trisulphide and iodine in the ratio $As_2S_3 : 6I$ until two-thirds of the material had passed over, the distillate was found to contain 58·63 per cent. of free iodine, 40 per cent. of arsenious iodide, and 1·37 per cent. of sulphur; the residue consisted of 55·32 per cent. of arsenious trisulphide and 44·04 per cent. of arsenious iodide. When in place of the former, a mixture of arsenious iodide and sulphur in the ratio of $2AsI_3 : 3S$ was employed, and the distillation continued until half the material had passed over, the distillate contained 69·44 per cent. of free iodine, 28 per cent. of arsenious iodide, and 2·56 per cent. of sulphur. These experiments show that whilst a mixture of arsenious trisulphide and iodine is converted at moderate temperatures into arsenious iodide and sulphur, these products again react at higher temperatures, reproducing their generators. If the distillate, rich in iodine, is sealed up in a glass tube, which is slightly inclined so that the distillate occupies the higher portion of the tube, and gently heated in a water-bath to a temperature of about 72°, a dark-brown liquid which solidifies on cooling trickles to the bottom of the tube. By repeated liquations in sealed tubes this dark-brown mass becomes perfectly homogeneous, crystallising in hard, brittle plates of a greyish-black colour, and dull lustre. The pure substance melts at 72°, and is represented by the formula $SI_6,2As_2I_3$. On pulverising, it forms a reddish-brown powder which by exposure to the air rapidly loses iodine, whilst the residue, consisting of a mixture of arsenious iodide and sulphur, assumes a bright-red colour.

On fusing a mixture of arsenious trisulphide with iodine in the ratio $As_2S_3 : 4I$, the iodine reacts with only two-thirds of the arsenious trisulphide present. When, as not infrequently happens, the arsenious trisulphide contains arsenious acid, there remains behind, after fusion with iodine and treatment with carbon bisulphide, an insoluble pale-yellow powder of the formula $2As_2S_3,3(AsI_3,As_2O_3)$. This substance can also be prepared by heating a mixture of arsenious trisulphide (1 part) and arsenious iodide (0·2 part) with a large excess (8 to 10 parts) of arsenious iodide, or by heating a mixture of arsenious iodide (4 mols.) with arsenious trisulphide (1 mol.) with free access of air. Under the microscope, the compound appears to be indistinctly crystalline. On gently heating it, arsenious iodide first sublimes, then arsenious acid, and lastly arsenious trisulphide.. The compound is completely dissolved by solutions of potash and ammonia, and is readily decomposed by the common mineral acids and by boiling water. G. T. M.

Silicon. By H. W. Warren (*Chem. News*, **57**, 54).—The following is a new method of preparing silicon. Small bars of "silicon-eisen" are suspended in dilute sulphuric acid from the positive pole of a battery of two ferric chloride cells and are in contact with a platinum plate forming the negative pole. The iron dissolves and leaves a residue of graphite, silica, and amorphous silicon, which is heated to redness in a stream of carbonic anhydride, and then to a full red heat in a closed iron tube with some zinc; the zinc button obtained in this manner is dissolved in hydrochloric acid, when crystalline silicon remains undissolved; by heating the amorphous silicon at a full white heat with aluminium instead of zinc, graphitoïdal silicon is obtained. When an alloy of aluminium and silver is heated to an intense white heat with potassium silicofluoride, small quantities of silicon are produced in the form of a bright reddish-brown powder. D. A. L.

Silver Suboxide and the Action of Potassium Permanganate on Silver. By C. Friedheim (*Ber.*, **21**, 307—318).—The first part of this paper is devoted to a criticism of v. d. Pfordten's latest communication on this subject (this vol., p. 221), and, in particular, attention is drawn to the fact that he no longer insists that the substance in question is silver suboxide, but only that it is not metallic silver. Referring to the statement that silver is dissolved by water acidified with sulphuric acid and exposed to the air, the author again states that the metal could not be detected in the solutions at the end of each experiment (compare Abstr., 1887, 1079). The action of permanganate has been studied under new conditions in an apparatus so contrived that a solution of permanganate acidified with dilute sulphuric acid placed in one bulb could by means of a connecting tube be brought in contact with a silver mirror in a second bulb after the bulbs and contents had been heated at 50° and at 100° respectively for 4 to 5 hours, whilst the apparatus was connected to a Töpler-Hagen's mercury pump, and then allowed to cool. Various strengths of permanganate were used, and in one experiment spongy silver was employed, but the results in every case showed that the permanganate acted at once on the silver and completely dissolved it. Experiments with the acidified permanganate solution *per se* showed that, on boiling, a decomposition occurred with the separation of an ochre-yellow or black oxide of manganese according to the concentration of the solution, and that this decomposition also occurred, although to a much smaller extent when the solution was heated at 40—50° for 4 to 5 hours in a vacuum. On this account, v. d. Pfordten's experiment of treating silver with a boiling acidified permanganate solution in a current of carbonic anhydride was not repeated, but in its stead the experiment in a vacuum was modified to the extent of filling the cold vacuous apparatus with pure carbonic anhydride (free from air) under pressure; connection was then made between the bulbs, with the result that the silver dissolved as before.

In reply to other objections to the author's views (*loc. cit.*) raised by v. d. Pfordten, it is pointed out that the complete dissolution of the latter's preparation (before ignition) in nitric acid does not disprove the presence of organic matter, since many organic substances are completely soluble in nitric acid. Again, the statement that no case is known in which impurity in the silver hinders amalgamation is met by an experiment in which an intimate mixture of finely divided silver and magnesia, obtained by adding calcined magnesia to a neutral solution of silver nitrate and igniting the precipitate, was shaken continuously with mercury for eight hours with the result that 1·149 gram of silver was dissolved and 0·8322 gram remained in the residue; hence v. d. Pfordten's argument, based on the fact that his substance underwent no change when shaken with mercury, is open to criticism. Finally, the change of colour from black to grey occurring when the so-called suboxide is treated with sulphuric acid or solutions of indifferent salts (*Ber.*, **20**, 1470, 3379) is paralleled by a similar change under like conditions in the colour of metallic silver precipitated from an ammoniacal solution of silver chloride by zinc, or from neutral silver solutions by other metals (Vogel, *Ber. Berl. Akad.*, 1862, 289). On these grounds, and without contesting the question of the existence of silver suboxide, the author maintains that v. d. Pfordten's substance is not this compound, but a mixture of finely divided silver with more or less silver oxide or organic matter.

W. P. W.

Lead Slags. By M. W. Iles (*Chem. News*, **67**, 4—7, 18—19, 37—38, 43—45, 57—58).—This communication contains the results obtained, and observations made in a very extensive investigation into the character and composition of lead slags. The sp. gr. of lead slags varies from 3·3 to 4·16, the best slags having a density of 3·4 to 3·65. Iron, barium, and lead cause high sp. gr.; aluminum, silica, and lime low gravities. All good slags are as a rule more or less perfectly crystalline; slow cooling favours crystallisation, sudden cooling impedes crystallisation or even stops it altogether, hence the crusts of pots of slag are devoid of crystalline structure. Well-crystallised slags have definite fusing points, and are more brittle than the imperfectly crystalline slags, and are only partially soluble in strong acids; the form of crystallisation serving as an important indication of the quality of a lead slag. Slags cooled by pouring into water are amorphous, have their fusing point lowered, resemble obsidian in appearance, and when pulverised are completely dissolved by hydrochloric acid. The author takes advantage of this property in taking and preparing samples for analysis; the crust of the pot of slag is thrown aside, a steel bar is thrust about 2 inches deep into the molten slag and then plunged into water. The outside rims of pots of slag are subject to rapid cooling. The colour of lead slags is almost always black or a dark shade. Lustrous black and the darkest slags contain most iron, this element, however, sometimes imparts a reddish tint, sometimes a slight greenish cast; lime tends to lighten the colour, giving the slag a stony or earthy appearance; large quantities of manganese give a reddish to amethystine hue, and when associated with 20 per cent. or more of lime, the slag has very often a resinous colour. Zinc in the presence of alumina, manganese, and much silica produces a porcelain or obsidian-like slag, whilst some very siliceous slags have a greenish cast. The lustre of lead slags is rarely pearly, often resinous, submetallic splendent, and pitchy; most are vitreous with the exception of high iron and high lime slags.

Both very viscid and very fluid slags are undesirable, inasmuch as the former retain globules of matte and metal, whilst the latter do not come sufficiently in contact with the ore, especially if it is in somewhat coarse lumps. Silica is the great cause of viscosity, whilst iron and manganese increase the fluidity of a slag, but fluidity due wholly to iron is liable to cause an iron crust, and so occasion loss. Lime may or may not make a fluid slag, most high lime slags, however, flow smoothly. Fusibility is a very important property of a slag, and is increased by iron, manganese, lime, and by alumina if the silica is low, and rarely or never by manganese and zinc. It is diminished by silica and by alumina in presence of much silica. Refractory slags arise either from insufficient temperature or from injudicious combination of the charges. The closer certain recognised types are approached, the greater will be both the fusibility and fluidity of a slag. Increasing the number of elements in a slag generally makes it more fusible, hence mixing different ores is advantageous; this remark, however, does not apply to zinc, aluminium, and magnesium: the latter element for some unaccountable reason occasions great loss of silver.

All lead slags are magnetic, the author attributing this property to the presence of iron silicates and sulphides. The brittleness of these slags depends on the number, kind, and amount of the bases present; generally silica causes toughness, and bases brittleness, although the latter is not always true. Slags with less than 34 per cent. of silica are usually brittle, whilst those containing as much as 35 to 40 per cent. are tough, unless there is little iron and much lime (22 to 30 per cent.). Whenever there is much matte produced or when zinc is present in the ore, it is best not to have very brittle slags. Brittle slags are generally free from both silver and lead. Lead slags consist mainly of iron and calcium silicates, manganese, however, is frequently present, so are also zinc, aluminium, barium, and magnesium, but the last four are to be avoided as much as possible. Incidental constituents of lead slags are silver, lead, potassium, sodium, phosphorus, sulphur, sometimes copper, nickel, and cobalt; whilst Leadville slags frequently contain vanadium. In abnormal slags, quartz, ferric oxide, and quicklime are sometimes found. Delicate needles containing lead and sulphur are observed in the blistered cavities in the crust of pots of slags.

The author does not approve of decomposing the slags by fusion with sodium carbonate and nitrate in a platinum crucible, but if such a method is resorted to, the pulverised slag should be first treated with hydrochloric acid, evaporated to dryness, more hydrochloric acid added, filtered, and then fused with sodium carbonate; or, better, fuse the slag directly with potash in a silver crucible, or if silver is also to be determined, in a platinum crucible heavily plated with gold. The method generally followed by the author is to take the sample in the way already noted, pulverise and moisten about half a gram with water, add concentrated hydrochloric acid, and digest with a few drops of nitric acid, the silica can then be separated perfectly free from iron in the usual manner. Iron is determined by permanganate, calcium as oxalate or volumetrically, manganese by the bromine or zinc oxide methods, other constituents by the usual methods.

The success of smelting siliceous ores depends on the economic use of lime, iron, and manganese as fluxes, whilst the life or campaign of a furnace is greatly influenced by the judicious selection of slags; such inconveniences as the accumulation of silica, or iron, charcoal, coke, zinc, or lead crusts may be eliminated by the use of suitable slags for some time. Slags must of course be varied to suit the impurities in the ores to be dealt with, but from the author's experience and the careful and complete analyses of 100 slag samples, the results of which are given in a table, it is concluded that certain definite "slag types," or slags having some well-defined composition and a distinct crystalline form exist, and that the nearer slags in general approach to any of these types the more effectual they are. Taking the important constituents lime, iron and manganese, and silica, it is observed that the best slags range within the following limits per cent.: SiO_2 31 to 36, Fe + Mn 23 to 30, CaO 14 to 25: whilst the slags doing the best work and ensuring the longest campaigns do not vary beyond SiO_2 31 to 34, Fe + Mn 24 to 27, CaO 14 to 25. The limits SiO_2 26 to 41, Fe + Mn 18 to 35, CaO 5 to 35, would include all lead slags.

The seven types laid down by the author include practically every known slag which is well adapted for melting argentiferous lead, and are composed as follows as regards the most important constituents:—

Types.	A.	B.	C.	D.	E.	F.	G.
CaO..........	6	10	12	16	20	24	28
FeO + MnO...	52	45	50	34	40	33	27
SiO_2..........	32	35	28	34	30	33	35

Type A. Crystallises in rectangular plates; but is not adapted to lead melting as the iron is too high, the lime too low.

Type B. Forms generally small, rhombic plates more or less thickened and characterised by well-defined striations. This type of slag will keep the furnaces in good condition, it gives large yields, but is liable to cause large losses of lead and silver; it is not a bad slag in localities where limestone is dear.

Type C. Is black and distinctly crystalline, and has the formula $6FeO,3SiO_2 + 2CaO,SiO_2$ assigned it. It is highly recommended where iron flux is abundant, and the ores carry much zinc.

Type D. Can be represented by the formula $5FeO,4SiO_2 + 3CaO,2SiO_2$; it crystallises in more or less translucent, flattened prisms often with an abrupt arrow-shaped termination. It is well adapted to the treatment of siliceous and very impure ores.

Type E. Corresponds to the formula $6FeO,3SiO_2 + 4CaO,2SiO_2$; it crystallises in monoclinic prisms. This is an excellent slag and very economical where the fluxes are easily obtained.

Type F. This is a black, lustrous, distinctly resinous slag. The crystals are rectangular prisms, remarkably translucent and even transparent when there is a little manganese present; the crystals are frequently indented. It is very friable.

Type G. Crystallises in cubes. It is the best slag known for the treatment of very siliceous ores, and has been found successful with ores containing large quantities of baryta, alumina, and zinc. Generally slags intermediate or differing widely in composition from the above types, having botryoidal, pectolitic or wavellitic crystalline forms, or those which are devoid of crystalline structure, may be considered abnormal and untrustworthy for smelting purposes. Hexagonal crystals indicate too high a percentage of lime. Slender needles result from fluxing highly siliceous ores with lime, and are accompanied by great loss of silver, but they contain no lead.

The proportion of lime seems to exert some influence on the crystalline structure of slags. The use of charcoal increases the tonnage, but generally with an increased loss of silver. These results show that certain ratios should exist between the silica and the bases of a slag, and that lime exerts a great cleansing influence on slags; but the problem why one slag is good and another of similar composition bad still remains to be answered. The author points out that loss of silver is due neither to the dissemination of globules of matte nor to the influence of manganese. D. A. L.

Crystallised Halogen Salts of Mercury. By W. SIEVERS (*Ber.*, **21**, 647—652).—Mercuric bromide is obtained in tetragonal plates when an excess of bromine is added with agitation to a slightly acid solution of mercuric nitrate of sp. gr. 1·197; hypobromous acid being formed in the reaction as noticed by Spiller (*Chem. News*, **6**, 249). The chloride prepared in like manner forms slender needles. Mercuric iodide is obtained in red, tetragonal plates by adding to a boiling solution of mercuric nitrate rather more iodine than it can dissolve, and boiling for some time with constant replacement of the evaporated water.

A mixture of mercuric and mercurous chlorides is obtained by the action of chlorine on a solution of mercurous nitrate; this is washed with hot water to remove the mercuric salt, and the amorphous mercurous chloride crystallised from mercurous nitrate solution, when it forms yellowish-white, tetragonal plates. Crystallised mercurous bromide and iodide have been already prepared by this method by Stroman (this vol., p. 111). A. J. G.

Ferric and Aluminium Phosphates. By P. HAUTEFEUILLE and J. MARGOTTET (*Compt. rend.*, **106**, 135—138).—Glacial phosphoric acid at 100° dissolves 15 per cent. of ferric oxide or 8 per cent. of alumina, and if the solutions are kept at this temperature they deposit distinct crystals which are readily decomposed by water. They have the composition $Fe_2O_3,3P_2O_5 + 6H_2O$ or $Al_2O_3,3P_2O_5 + 6H_2O$. The ferric compound forms pinkish, rhombic plates, derived from a monoclinic prism; the aluminium compound forms colourless, prismatic crystals with longitudinal extinction.

If the solution is heated rapidly to 150—200°, and is kept at this temperature, the crystals contain only 4 mols. H_2O, and are not readily attacked by water or alcohol. The iron salt forms pinkish, nacreous, rectangular lamellæ, which act strongly on polarised light; the aluminium salt forms birefractive needles grouped in bundles.

Above 200°, the solution deposits crystals at a temperature which is lower the greater the proportion of basic oxide present. In all cases they have the composition $Fe_2O_3,3P_2O_5$ or $Al_2O_3,3P_2O_5$, but the form of the iron salt depends on the temperature at which crystallisation takes place. At 200—250°, it forms short, channelled, rhombic prisms; from 250° to incipient redness, fusiform, triclinic crystals; at a red heat, long, monoclinic prisms, sometimes with an almost square orthogonal section, and usually terminated by a rhombic face at an acute angle with the edge of the prism.

At 200°, the aluminium phosphate separates in tetrahedra with curved faces, without sensible action on polarised light; at 250°, the crystals are octahedra, frequently modified by faces of the cube. This form is stable up to a red heat. If the phosphate crystallises at a red heat, or is obtained by the action of phosphoric acid on corundum, it separates in cubes which are not modified, but are frequently macled. From these results, it seems that the anhydrous aluminium phosphate always crystallises in the regular system, but the exact form depends on the temperature. These differences are comparable with the differences observed in the case of ferric and silicon phosphates. C. H. B.

Volume and Carbon Contents of the Gas Evolved during Solution of Iron in Acids. By H. BÄCKSTRÖM and G. PAIJKULL (*Zeit. anal. Chem.*, **26**, 683—689).—That different kinds of iron evolve different volumes of gas when dissolved in acid was ascertained by Bergman in 1781, and these differences were connected by Vandermonde, Berthollet, and Monge, with the differences in the amount of carbon present.

The authors have determined the total volume of gas, and the quantity of carbon in it, from 14 samples of iron containing carbon (total) ranging from 0·11 to 4·24 per cent. As a general rule, the more highly carburetted the iron, the smaller is the volume and the greater the carbon-contents of the gas evolved, but the relation is not a quantitative one in either case. No definite fraction of the combined carbon is evolved as a gaseous hydrocarbon. Part of the carbon invariably remains dissolved in the acid as an organic substance capable of reducing permanganate, so that the results of titration are too high as well as variable. Bergman asserted that sulphuric and hydrochloric acids evolved equal volumes of gas, but in a special experiment on a white cast iron containing 3·87 per cent. of carbon, a volume of gas larger, and containing more carbon, was obtained with hydrochloric acid than with sulphuric acid of corresponding strength.

It is well known that hardened steel leaves less residue than unhardened when dissolved in acids. Cold hammered steel behaves like hardened steel. The latest view of the constitution of steel is that it contains a true carbide of iron forming a mass of cellular texture, the pores of which are filled with pure iron. According to Osmond and Werth, the so-called cement-carbon (*Cement-Kohlenstoff*, *carbone de recuit*) is that which exists in the carbide in combination with iron, whilst the hardening-carbon (*Härtungs-Kohlenstoff*, *carbone de trempe*) exists in solution in the iron disseminated in the cellular nuclei. The latter may therefore be expected to be converted more or less into gaseous hydrocarbons, whilst the former would more or less remain undissolved on treatment with acid. It is found that hardened steel gives both a larger volume of gas, and one richer in carbon than the same steel before hardening. It seems as though almost the whole of the hardening carbon is evolved as gas. The effect of cold hammering is, however, both as to volume of gas and amount of carbon, exactly the reverse. M. J. S.

Action of Sea-water on Cast Iron. By C. N. DRAPER (*Chem. News*, **56**, 251).—A specimen of cast iron, weighing 557·31 grams, and measuring 85 mm. × 52 mm. × 20 mm., was broken from a rail which had been exposed to the alternate action of sea-water and the atmosphere for about 50 years. The lateral surfaces were slightly coated with oxide, and the upper surface consisted, to a depth of 7 mm., of a brownish-grey, graphitoïdal substance, amounting to 67·59 grams, and containing 23·6 per cent. of carbon along with much unoxidised iron, presumably existing as FeC_3. The graphitoïdal substance was easily removed from the specimen with a knife, leaving a clean, bright, metallic surface exposed. This operation was accompanied by a distinct rise in temperature. D. A. L.

Influence of Phosphorus on Iron. By L. SCHNEIDER (*Dingl. polyt. J.*, **266**, 378—382).—According to Cheever, the variable effect of phosphorus on iron is explained by assuming that the phosphorus is present in the metal in two forms, as "phosphate" and "phosphide," which influence the properties of iron in different ways. This assumption is based on the analytical results obtained in a series of experiments in which the iron was treated with a cold ammoniacal solution of cupric chloride, the residue being digested with an alkaline solution of ammonium oxalate, or shaken for five minutes with a 1 per cent. solution of hydrochloric acid, and the phosphoric acid determined in the solution. Cheever assumes that the small amount of phosphide existing in the metal completely resists the action of cupric chloride, and that the complete solution of all phosphates formed from phosphides at a red heat is effected either by a treatment with a 1 per cent. solution of hydrochloric acid for five minutes, or by the action of an ammoniacal solution of ammonium oxalate.

The author criticises Cheever's method of examination, and the conclusions deduced therefrom. He shows that iron phosphide in iron is affected by cupric chloride in the cold, and if the solution is quite neutral the phosphoric acid obtained by the oxidation of the phosphide remains in the residue, from which it may be subsequently extracted with ease by weak acids. D. B.

Vapour-density of Ferric Chloride at Various Temperatures. By W. GRÜNEWALD and V. MEYER (*Ber.*, **21**, 687—701).—In these experiments, sublimed ferric chloride was used. The estimations were made in a slightly modified form of V. Meyer's apparatus, in which the bulb, 45 mm. in diameter, was reduced to a length of only 125 mm., whilst the whole apparatus was 670 mm. high; by this means, the whole of the bulb acquired the temperature of the bath. For greater convenience in filling with nitrogen, a thin tube was fused into the bottom of the bulb, bent so as to follow the shape of the bulb and stem until the side tubes were nearly reached, then bent at right angles to connect with the nitrogen supply.

A new device of Meyer and Biltz for the introduction of the substance is also described:—On the stem, opposite to, but just below the delivery tube, a short side tube is fused; through this passes a glass rod whose end projects across the stem; the joint between rod and side tube being made with well-fitting caoutchouc tubing. The little bottle containing the substance rests on the end of the rod; when the bulb has attained the required temperature, the rod is slightly withdrawn, and the bottle falls into the bulb.

Four determinations at 448° (in sulphur vapour) gave a density of 10·487, whilst that required by the formula Fe_2Cl_6 is 11·2. After the estimation, the contents of the bulb did not give the slightest reaction for ferrous salt. Experiments at a lower temperature were out of the question, as even in these the vaporisation was rather slow.

At 518° (in vapour of phosphorus pentasulphide), three experiments gave a vapour-density of 9·569; about $\frac{1}{10}$ of the iron was found to be in the ferrous condition after the estimation.

At 606° (in vapour of zinc chloride), in a smaller apparatus, six experiments gave a mean vapour-density of 8·383; about $\frac{1}{8}$ of the iron was in the ferrous state at the close.

The determinations at higher temperatures were effected in platinum apparatus heated in a Perrot's gas furnace. The mean of three estimations at about 750° gave a vapour-density of 5·406, whilst about $\frac{1}{3}$ of the iron was found to be in the ferrous state at the close of the experiments. At about 1050°, the numbers obtained for the density were 5·3 and 4·9; $\frac{1}{5}$ and $\frac{1}{3}$ of the iron being respectively found in the ferrous state. The results at 1300° were practically identical with those at 1050°. As it seemed probable that the lower results in the higher temperature experiments might be due to the action of the platinum on the ferric chloride, experiments were made in platinum apparatus at about 600°, but the results obtained were in agreement with those previously got in glass.

With regard to the amounts of ferrous salt observed at the end of the experiments, it must be remembered that this does not show the amount of dissociation that occurred at the temperature of the experiment, inasmuch as recombination occurs on cooling.

Experiments in a chlorine atmosphere at the temperature of boiling sulphur and boiling phosphorus pentasulphide respectively, gave practically the same results as those in an atmosphere of nitrogen.

From these results, it follows that ferric chloride does not at any temperature show a vapour-density sufficiently high for the molecular formula Fe_2Cl_6, whilst at 750° and 1077° numbers were obtained not far removed from 5·6, the calculated vapour-density for the molecular formula $FeCl_3$. A. J. G.

Use of Hydrogen Sulphide to Purify Nickel and Cobalt. By H. Baubigny (*Compt. rend.*, **106**, 132—135).—The only possible method of separating nickel and cobalt by means of hydrogen sulphide is to saturate the solution of the sulphates with the gas at 0°, and heat to 100°. Nickel sulphide is precipitated, but cobalt sulphate is not decomposed. The precipitate, however, always contains a notable proportion of cobalt even when the quantity of free acid is almost sufficient to prevent the precipitation of the nickel. Dellf's method of precipitating cobalt as sulphide from the acetate by mixing a solution of the nitrates or sulphates with a quantity of sodium acetate not quite sufficient to convert all the cobalt into acetate, is not satisfactory, since a considerable proportion of the nickel is precipitated at the same time. C. H. B.

Alloy of Titanium, Silicon, and Aluminium. By L. Lévy (*Compt. rend.*, **106**, 66—68).—10 grams of titanium, 35 grams of aluminium, 35 grams each of fused sodium and potassium chlorides, were heated in a Perrot's furnace in a porcelain crucible enclosed in a crucible brasqued with charcoal and rutile, a current of dry hydrogen being passed into the inner crucible. The product was treated with water and then with dilute acid, and a residue was obtained consisting of lustrous, steel-grey lamellæ, with angles of 90°, very brittle, and good conductors of heat, sp. gr. at 16° = 3·11. They do not alter in air or nitrogen oxides at the ordinary temperature, but tarnish when heated, and burn if heated in oxygen. They are not attacked by vapours of sulphur, selenium, phosphorus, or arsenic, but burn in chlorine or in vapour of iodine or bromine, especially the former. Liquid bromine, however, is without action. Superheated steam and cold fuming nitric acid have no action, but hot nitric acid attacks the crystals slightly. Hydrochloric and sulphuric acids act somewhat in the cold and more readily when heated. The crystals burn when heated in hydrogen chloride, and dissolve readily in aqua regia, but are not dissolved by hydrobromic and hydriodic acids, or by mixtures of these acids with nitric acid. Sulphuric acid and calcium fluoride have little action, and potash only partially dissolves the crystals in the cold, but dissolution is complete on heating, with evolution of hydrogen. The crystals have the composition Al 71·06; Ti 26·65; Si 2·19; loss (? C) 0·10, which agrees with the formula (Ti : Si)Al_4, and hence it is probable that they are mixtures of the isomorphous compounds, $TiAl_4$ and $SiAl_4$.

If zinc or magnesium is substituted for aluminium, no crystals are obtained. C. H. B.

Titanium Trioxide. By A. Classen (*Ber.*, **21**, 370—372).—The action of hydrogen peroxide on titanium dioxide (compare Piccini, Abstr., 1882, 808; 1883, 1054; Weller, Abstr., 1883, 295) has been studied by the author, who recommends the following method for obtaining the product:—Pure titanium chloride is added drop by drop to dilute alcohol, and the clear and very dilute solution is treated with a large excess of hydrogen peroxide. Ammonia, ammonium carbonate, or aqueous potash is added to the solution with the production of a yellow or, in the case of ammonia, of a reddish-yellow liquid, which after some time yields a yellow precipitate. This is allowed to subside, the clear solution siphoned off, and the precipitate repeatedly washed by decantation; the compound, however, tends to retain water and salts in considerable quantities. When dried on a tile, it approximates to the composition $TiO_3 + 3H_2O$.

W. P. W.

Antimony Pentachloride. By R. Anschütz and P. N. Evans (*Proc. Roy. Soc.*, **42**, 379—387; compare Trans., 1886, 379).—The authors find that, contrary to the statement of Daubrawa (this Journal, 1877, ii, 406), $SbOCl_3$ is not formed when water is added to antimony pentachloride, nor is any hydrogen chloride evolved. The antimony pentachloride is best dissolved in chloroform, and the calculated amount of water added. Under these circumstances a crystalline substance, $SbCl_5,H_2O$, soluble in chloroform, is obtained, melting at 87—92°. It is very hygroscopic, and diliquesces to a clear liquid, which crystallises over sulphuric acid in broad crystals, described by Daubrawa as the oxychloride. When distilled, it gives $SbCl_5,SbCl_3$ and a waxy residue.

A chloroform solution of antimony pentachloride, when heated with water in a sealed tube, gives antimony trichloride and phosgene gas. Phosgene gas is also produced by heating a chloroform solution of the monohydrate at 100°.

Antimony pentachloride tetrahydrate can be produced in the same way as the monohydrate. It is a crystalline mass, insoluble in chloroform. By adding anhydrous oxalic acid to a chloroform solution of antimony pentachloride, the authors obtain a substance, $Sb_2Cl_8C_2O_4$, probably $C_2O_2(O{\cdot}SbCl_4)_2$. It crystallises from chloroform in tables melting at 148·5—149°, and is decomposed by water with liberation of oxalic acid.

The difference in behaviour with carbon compounds between phosphorus pentachloride and antimony pentachloride is attributed to the property of the latter of combining with water instead of decomposing it. H. K. T.

Redetermination of the Atomic Weight of Platinum. By W. DITTMAR and J. MCARTHUR (*J. Soc. Chem. Ind.*, 6, 799—803).—The value Pt = 194·8 which Seubert (Abstr., 1881, 514) deduced from his analyses of platinochlorides, is too low; his own analyses, if properly interpreted, show that the true value lies, by a considerable fraction of a unit, higher. According to the authors' analysis of potassium platinochloride, the true "Pt," although probably a shade below, lies close to 195·5. Taking "Pt" as meaning the number which must be substituted for Pt in the calculation of the ratios 2KCl : $PtCl_6K_2$; 2KCl : Pt, &c., in order to obtain the correct factors for reducing analytically obtained platinochloride to potassium chloride, &c., even the number 195·5 is too low, 196 affording in general a better approximation. But Pt if taken in this sense is no constant at all. Those factors must be determined directly by standard experiments. The results of the authors' own standard experiments are given and contrasted with the theoretically calculated ratios in the subjoined table. The entries "Ta" refer to Tatlock's methods; those "F" to the authors' form of Finkener's method described in detail in the original paper, and those marked "N" to the usual platinum process for the determination of ammonia:—

Method.	Theoretical factors.				Dittmar and McArthur's empirical factors.	Notes.
	Symbols.	Values calculated for				
		Pt = 194·8	195·5	196		
Ta	2KCl : $PtCl_6K_2$	0·30707	0·30665	0·30633	0·30627	(1)
Ta	2KCl : Pt	0·76571	0·76307	0·76112	0·76016	(2)
F	2KCl : Pt	0·76571	0·76307	0·76112	0·76084	(1)
N	$2NH_4Cl$: $PtCl_6(NH_4)_2$.	0·24123	0·24084	0·24057	0·23890	(3)
N	$2NH_4Cl$: Pt	0·54934	0·54737	0·54598	0·54590	(4)

Notes. (1) Refers to the potassium chloride in the substance, (2) to that in the platinochloride precipitate, and (3) and (4) to the ammonium chloride to be determined, not to that contained in the platinochloride precipitate. D. B.

Hydroxylamine Platinum Bases. By H. ALEXANDER (*Chem. Centr.*, 1887, 1254—1255).—As the platinum bases mentioned below are all explosive, the platinum and chlorine cannot be determined by heating the compound. The platinum was determined by moistening a quantity of the substance with concentrated sulphuric acid in a platinum capsule, evaporating off the acid and finally dispelling any remaining acid by the addition of ammonium carbonate. The chlorine was determined by distilling the compound with sulphuric acid, and passing the resulting hydrogen chloride into a solution of silver nitrate.

Platoso-dihydroxylamine hydrochloride, $Pt(NH_3O{\cdot}NH_3OCl)_2$, which Lössen has already described, is obtained by the action of potassio-platinous chloride on hydroxylamine hydrochloride. Strong bases precipitate *platoso-dihydroxylamine hydroxide*, $Pt(OH)_2,4NH_3O$, from solutions of the chloride. The oxalate, $PtC_2O_4,4NH_3O$, is prepared from neutral potassium oxalate and the chloride; an acid salt does not seem to exist. *Platino-dihydroxylamine sulphate*, $PtSO_4,4NH_3O + H_2O$, can be prepared from this oxalate by the action of weak sulphuric acid; the sulphate is more easily prepared from the free base and sulphuric acid. A phosphate was obtained, but no nitrate.

Platoso-dihydroxylamine hydrochloride platinous chloride is prepared by the addition of platinous hydrochloride to the chloride.

Platoso-hydroxylamine hydrochloride, $Pt(NH_3OCl)_2$, is formed by the action of hydrochloric acid, on either platino-dihydroxylamine hydrate when warm, or on the corresponding chloride.

The compound formed by the action of ammonia on platinous hydrochloride and on platoso-hydroxylamine hydrochloride, which has been described by Jörgensen, the author regards as platoso-hydroxylamine ammonium chloride, $Pt(NH_3O{\cdot}NH_3Cl)_2$.

The double salt, $Pt(NH_3O{\cdot}NH_3Cl)_2,PtCl_2$, is obtained from platinous hydrochloride and platoso-hydroxylamine ammonium chloride, as well as from the above-named mixed chlorides and potassio-platinous chloride.

Free hydroxylamine acting on platinous chloride gives rise to the compound $OH{\cdot}PtCl,4NH_3O + 2H_2O$, which explodes at 140—150°. Another compound which may be regarded as platinum nitrogen chloride, PtNCl, together with the double salt,

$$2(OH{\cdot}PtCl,4NH_3O) + Pt(OH)_2,2NH_3O, \text{ or } 2[Pt(OH)_2,4NH_3O] + PtCl_2 + 2NH_3O.$$

were also obtained.

Free hydroxylamine acting on platinous hydrochloride gives rise to a compound corresponding approximately with the formula $PtCl_2,4NH_3O$, and by its action on potassio-platinous chloride to a base $Pt(OH)_2,2NH_3O$, which has not been obtained quite pure as yet.

J. P. L.

Ruthenium Oxides. By H. Debray and A. Joly (*Compt. rend.*, **106**, 100—106).—The authors prepared crystallised ruthenium dioxide by heating the amorphous oxide in a vacuum or by heating the metal in oxygen. It forms quadratic prisms with the faces m, h', a', and b'. The ratios being $b : h :: 1000 : 692{\cdot}43$, and hence is isomorphous with cassiterite and rutile. The faces in the zone $m\ h'$ are often striated as in those minerals, and very frequently the crystals are macled after the cassiterite and rutile types.

When heated to bright redness in a muffle, ruthenium absorbs oxygen, but after some time absorption takes place very slowly, and the metal is never fully oxidised to the dioxide. If, however, the product is powdered and again heated, the dioxide is obtained crystalline, with an indigo-blue colour. The authors were unable to obtain the sesquioxide in the manner described by Claus.

When ruthenium is heated in oxygen at a temperature above the melting point of silver, it is entirely converted into crystalline products, and a portion volatilises and condenses in crystals. If the current of gas is rapid, the odour of ozone or ruthenium peroxide is perceived, and a certain quantity of the peroxide can be condensed in a flask cooled by ice. The inside of the tube is lined with ruthenium dioxide and a small quantity of a black substance which seems to contain more oxygen than the dioxide. The products are similar to those obtained when ruthenium peroxide and nitrogen are passed through a red-hot porcelain tube, and they are distributed in the same manner. The dioxide is found in the cooler parts of the tube, which indicates that the peroxide formed at about 1000° decomposes at a lower temperature. At temperatures above 1000°, ruthenium dioxide has a considerable tension of dissociation, and in a vacuum is partially reduced to the metal, a small quantity of the peroxide being formed. At a bright red heat, the phenomena are similar.

The authors were unable to obtain an oxide lower than the dioxide.

Ruthenium peroxide is formed at about 1000°, and decomposes with explosion when cooled to 108°, but can be isolated by rapid cooling. It affords another instance of a compound which is decomposed by heat, and yet is formed at a high temperature. The crystallisation of the dioxide is a phenomenon of apparent volatilisation, and the formation of the peroxide is analogous to the formation of ozone, silicon hexachloride, silver oxide, hydrogen selenide or telluride, &c.

The formation of ruthenium peroxide, like the decomposition of water, is endothermic. C. H. B.

Mineralogical Chemistry.

A New Zealand Sulphur Island. By R. W. E. MACIVOR (*Chem. News*, **56**, 251—253).—White Island, in the Bay of Plenty, New Zealand, is part of the crater of a huge, submerged, conical volcano. Part of the island disappeared during the volcanic disturbances in New Zealand a year or two ago. The mineralogical and other characters of the place in 1883 were such as are general in volcanic regions; special features were heaps of gypsum with from 30 to 85 per cent. of sulphur, and curious hollow spheres, some as large as old-fashioned bombshells, consisting of an exterior crust of gypsum and a little sulphur, with transparent crystals of prismatic sulphur inside. There were active geysers and fumeroles sending out hydrogen chloride and steam, and ejecting with great violence transparent lumps of sulphur varying in colour from orange to a reddish-brown, although the sulphur deposited around the orifices was pale yellow and opaque; the depth of colour is due to selenium; some specimens contain as much as 1·75 to 2·1 per cent., which render it unfit for the manufacture of sulphuric acid. In the neighbourhood of the fumeroles there were many large holes full of thin, black, boiling mud consisting of clay, siliceous matter, gypsum, and iron pyrites suspended in strongly acid water containing more mineral matter than the water from the lake. Lake Hope, in the midst of the central amphitheatre, had a fairly uniform depth, but was unfathomable near the centre; its temperature was 68°; it was muddy in the centre, but transparent, and of blue-green colour elsewhere; the atmosphere over it was very irritating owing to the constant evolution of hydrogen chloride; the bottom of the lake wherever visible was covered with oblique crystals of selenite. Analysis of the water yielded the following results per 1000 parts:—

$FeSO_4$.	$Al_2(SO_4)_3$.	$CaSO_4$.	$MgSO_4$.	K_2SO_4.	Na_2SO_4.	Al_2Cl_6.
15·254	1·350	3·605	0·931	4·715	10·033	25·557

NaCl.	SiO_2.	HCl.	Water, &c.
11·950	0·67	149·876	776·059

It is suggested that the sulphur and hydrogen chloride result from the action of sea-water on hot beds of pyrites inside the mountain.

D. A. L.

Graphite from the Bagoutal Mountains, Siberia. By W. H. Collins (*Chem. News*, **57**, 36).—Four samples of graphite from this region were analysed and gave the following mean results per cent.:—C, 38·91; SiO_2, 38·83; Al_2O_3, 13·86; CaO and MgO, 2·12; Fe_2O_3, 4·52; loss and volatile matter, 1·77. This graphite is employed for crucible making with excellent results. It is somewhat similar in character to the graphite from the Stephanovsky mine. D. A. L.

Gold Quartz from the Transvaal. By P. Holland (*Chem. News*, **56**, 271—272).—The specimen weighed 18 grams; it was a greenish-grey, dark-coloured, massive quartz with iron-stained fissure. In sections, under the microscope, F. Rutley detected "allotriomorphous" quartz crystals, cubes of pyrites, gold, numerous liquid lacunæ, particles of mica, and patches, probably, of felspar. On heating in an open tube, sulphurous anhydride was given off. For analysis the mineral was decomposed with hydrofluoric acid, and gave the following numbers:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeS_2.	Au.	MgO.	K_2O.	Na_2O.	H_2O.	C.
92·86	2·86	1·22	0·27	0·03	0·18	1·40	0·41	0·58	a little.

D. A. L.

Braunite from Jakobsberg. By M. Schuster (*Zeit. Kryst. Min.*, **13**, 621—623, from *Tschermak's Min. Mitth.*, **7**, 443—451).—This mineral, discovered by Igelström (Abstr., 1887, 643) at the Jakobsberg manganese mines, Wermland, Sweden, has been subjected by the author to a careful crystallographical examination. Braunite, he finds, is not tetragonal, as stated by Igelström, but rhombohedral, tetartohedral, and isomorphous with iron glance and titaniferous iron ore. B. H. B.

Chrome Iron Ore in Australasia. By R. W. E. MacIvor (*Chem. News*, **57**, 1—2).—Chrome iron ore is found in New Zealand in two or three places, but chiefly near Nelson, in the middle island, where it is associated with serpentine and olivine rocks; it is obtained in three forms: (1.) *Massive crystalline* in highly crystalline black bands, showing on fracture distinct planes of octahedron, and containing from 52 to 65 per cent. of chromic oxide. (2.) *Massive amorphous*, brownish-black bands, longer, broader, and softer than the preceding, in which Cr_2O_3 = from 30 to 51 per cent. (3.) *Disseminated crystalline*, in which nodules of moderately constant composition, 56 to 69 per cent. Cr_2O_3, are more or less evenly distributed through the serpentine, forming in some cases as much as 90 per cent., in others only 20 per cent. of the rock, giving it the appearance of a conglomerate. On exposure to the air, the binding material disintegrates and the nodules are easily separated; in some cases, the preliminary weathering may be dispensed with.

Chrome iron ore is also found in New Caledonia, in New South Wales, in Queensland, and in Tasmania. D. A. L.

Genesis of the Plumbiferous Phosphates and Arseniophosphates of Roure and de Rosiers, Pontgibaud. By F. GONNARD (*Compt. rend.*, **106**, 75—77).—These minerals occur in the neighbourhood of apatite and lead carbonate. It is known that water containing carbonic anhydride will dissolve both lead carbonate and apatite, and it is probable, therefore, that the lead phosphate or arseniophosphate has been formed by the interaction of these substances or by the action of the water containing apatite on galena.

C. H. B.

Mineralogical Observations in Styria. By E. HATLE and H. TAUFS (*Chem. Centr.*, 1887, 1264—1365, from *Verh. geol. Reichanst.*, 1887, 226—228).—(1.) *Pharmacolite from Völleg.*—This mineral, which is new to Styria, has been found in large (5 mm.) crystals and in spheroïdal groups and crusts on iron pyrites, magnetic pyrites, and arsenical pyrites, blende, galena quartz, and calcspar; it contains—

As_2O_5.	CaO.	H_2O at 110°.	H_2O at red heat.	Total.
48·60	27·04	12·34	12·15	100·13

Albite in twin crystals has likewise been found in the neighbouring lead mine of Kaltenegg.

(2.) *Iron Deweylite from Kraubach.*—This scarlet-red mineral, obtained from serpentine in Leising, corresponds with the formula $10H_2MgSiO_4,Mg_2FeSiO_5 + 9H_2O$. As many other deweylites contain the same amount of water, the authors suggest the following general formula for deweylites:—

$$10H_2R''SiO_4,R''_3SiO_5 + 9Aq,$$

in which R'' = Mg, which is in part displaceable by Fe, Ni, &c.

J. P. L.

New Discoveries of Minerals. By H. v. FOULLON (*Zeit. Kryst. Min.*, **13**, 631—632, from *Verhdl. k. k. geol. Reichsanst.*, 1886, 464).—At Klausen, in Tyrol, a greenish-blue mineral has been found as a thin coating on mica-schist and quartzite, in association with gypsum, felsöbanyite, malachite, and allophane. This greenish-blue coating, undoubtedly of recent formation, is a mineral mixture, of which 54 per cent. consists of a hydrated copper sulphate, langite, $CuSO_4 + 4H_2O$, in all probability a product of the alteration of copper pyrites.

At the same locality, calcite of recent formation has been found. It occurs in an old adit-level, in the form of white or yellow imperfect crystals, and attains a thickness of 4 cm. In the Reussen lode, at Kuttenberg, in Bohemia, the rare mineral cronstedtite has recently been found in well-developed crystals. B. H. B.

Ilmenite from the Ardennes. By C. Klement (*Zeit. Kryst. Min.*, **13**, 626—627, from *Tschermak's min. Mitth.*, **8**, 1).—Ilmenite from the phyllite of Rocroi gave on analysis the following results:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	K_2O.	Na_2O.	Total.
2·14	52·21	1·83	3·52	27·16	13·60	0·43	0·23	0·19	101·31

Neglecting the admixed rutile and silicates, the formula of the ilmenite is $RTiO_3$, in which R = Fe,Mn in the proportion of 2 : 1.
B. H. B.

Synthesis of Pyrrhotine. By C. Doelter (*Zeit. Kryst. Min.*, **13**, 624—626, from *Tschermak's min. Mitth.*, **7**, 535—545).—The author has endeavoured to prepare magnetic pyrites (pyrrhotine) synthetically, and by means of analyses of the artificial mineral and of the pyrrhotine recently found at Schneeberg, in Tyrol, to elucidate the constitution of this mineral. The first experiment, in which ferrous chloride was heated with water containing sodium carbonate, and saturated with hydrogen sulphide, in a closed tube at 80° for three months, was unsuccessful, inasmuch as the pyrrhotine formed was decomposed on washing, a powder resembling limonite being produced. In the second experiment, ferrous chloride was treated under the same conditions in a closed rifle-barrel at 200° for 16 days. In consequence of the air remaining in the barrel, iron pyrites was formed as well as pyrrhotine; but when the filling of the barrel was effected in an atmosphere of hydrogen sulphide and carbonic anhydride, pyrrhotine was formed in small, hexagonal, brown, magnetic tablets, which on analysis gave results corresponding with the formula $Fe_{11}S_{12}$. A product similar in appearance was obtained on treating a mixture of ferrous chloride and zinc chloride in the same way at 200° for three weeks, the powder obtained giving on analysis results corresponding with the formula $R_{11}S_{12} = Fe_{21}ZnS_{24} = 2(Fe_{11}S_{12}) + ZnS$. Possibly this is a mechanical mixture of pyrrhotine and wurtzite. From these experiments, the author concludes that pyrrhotine is formed in nature at a low temperature, about 100°, from ferrous salts dissolved in water by the action of hydrogen sulphide in the presence of carbonic acid or reducing hydrocarbons. Further experiments were made in the dry way, ferrous chloride being heated in a stream of hydrogen sulphide in a glass tube from which the air had previously been expelled by a current of carbonic anhydride. Crystals having the formula $Fe_{11}S_{12}$ were obtained.

In conclusion, the author gives the following analysis of pyrrhotine recently found at the Schneeberg, in Tyrol:—

Fe.	S.	Co.	Total.
61·77	39·10	trace	100·87

These results correspond with the formula $Fe_{11}S_{12}$, or $10FeS + FeS_2$, a formula which was deduced from the analyses of all the artificial pyrrhotines prepared by the author. B. H. B.

Composition of Idocrase. By C. RAMMELSBERG (*Zeit. Kryst. Min.*, **13**, 640—642, from *Zeit. deutsch. geol. Ges.*, **38**, 507).—The recent analyses of idocrase (vesuvian), by v. Lasaulx, Ludwig, and Jannasch, have induced the author to analyse again the idocrase of Ala and Wilui, and to determine the formulæ with greater accuracy. The old theory of the general constitution of idocrase, $4R'_4SiO_4 + R'_6SiO_5 = R'_{22}Si_5O_{21}$, still holds good. It has, however, been simplified to a certain extent, since in idocrase $R'' : R'''_2 = 4 : 1$. The ratio of $R' : R''$, however, is variable, so that all varieties of idocrase may be divided into four classes, in which—

(1.) $R' : R'' = 1·66 : 4 = 1 : 2·4$
(2.) $R' : R'' = 1·33 : 4 = 1 : 3$
(3.) $R' : R'' = 1·00 : 4$
(4.) $R' : R'' = 0·5 \ : 4 = 1 : 8.$

Consequently the general formula is

$$R'_{22}Si_5O_{21} + n[(4R''_{11}Si_5O_{21})(R'''_{22}Si_{15}O_{63})], \text{ or } (4R'_4SiO_4 + R'_6SiO_5)n[4(4R''_2SiO_4 + R''_3SiO_5)(4R'''_4Si_3O_{12} + 3R'''_2SiO_5)].$$

To Class 1 belong the idocrase of Ala and Gleinitz, near Jordansmühl, in Silesia; to Class 2, those of Monzoni, Zermatt, Johnsberg in Silesia, Kedabek in the Caucasus; to Class 3, those of Vesuvius, Haslau near Eger; to Class 4, those of Wilui (in which the presence of boron was detected by Jannasch).

Idocrase and epidote are very similar in composition—

Epidote..............	$2R'_4SiO_4 + R'_6SiO_5$
Idocrase..............	$2R'_4SiO_4 + R'_6SiO_5$.

B. H. B.

Canadian Minerals. By B. J. HARRINGTON (*Zeit. Kryst. Min.*, **13**, 651, from *Trans. R. Soc. Canada*, 1886, 81).—The author gives the results of analyses of sodalite (I) from the nepheline-syenite of Montreal, and (II) from the Ice River, Rocky Mts.:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	Na.	Cl.	Total.	Sp. gr.
I.	37·52	31·38	trace	0·35	19·12	0·78	4·48	6·91	100·54	2·22
II.	37·50	31·82	0·01	—	19·34	0·27	4·61	7·12	100·67	2·29

The mineral, termed *huronite* by Thomson, from the diabase of Drummond Island, in Lake Huron, is found by the author to be an impure or altered felspar, probably anorthite. B. H. B.

Felspar and Olivine from Syria. By B. Doss (*Zeit. Kryst. Min.*, 13, 624, from *Tschermak's min. Mitth.*, 7, 461—534).—The author analysed two specimens of felspar from plagioclase-basalts; I, from Schuhba; II, from Chirbet Hôjet Sâlâ:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	$\underbrace{K_2O.\quad Na_2O.}$	Total.
I.	51·26	31·49	0·33	trace	13·13	0·45	3·60	100·26
II.	50·23	31·88	0·20	trace	14·60	0·26	3·44	100·61

Plagioclase I is a labradorite, with the ratio Ab : An = 1 : 2 (8 : 17); plagioclase II is a labradorite, with the ratio Ab : An = 2 : 5. The olivine in these plagioclase-basalt-lavas usually occurs in twin-crystals, ∞P being in some cases the twinning-plane. B. H. B.

Albite of the Kâsbek. By M. Schuster (*Zeit. Kryst. Min.*, 13, 614—615, from *Tschermak's min. Mitth.*, 7, 373—399).—The determinations of the direction of extinction on P in the theoretically pure albite of the Kásbek in the Caucasus, recorded by Bärwald (*Zeit. Kryst. Min.*, 8, 48), differ so entirely from those given by the author in his well-known work on the optical properties of the plagioclases, as to induce him to make a new investigation of this albite, using material chemically identical with that employed by Bärwald. His measurements of the angles of the crystals show that the discrepancy is caused by Bärwald having confused the right and left prisms.

B. H. B.

Anorthite from Saint-Clément. By A. Lacroix (*Zeit. Kryst. Min.*, 13, 646, from *Bull. soc. fran. min.*, 9, 46).—In the anorthite-gabbro of Saint-Clément, department Puy-de-Dôme, the author found the following minerals: titanite, idocrase, bright-green pyroxene, partly converted into actinolite, and anorthite twinned according to the albite and pericline law. The anorthite gave on analysis:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	Total.
46·05	35·10	18·32	(0·53)	100·00

As secondary minerals, there occur wollastonite, epidote, quartz, talc, and calcite. B. H. B.

Beryl from the Ifinger. By M. Schuster and R. Przibram (*Zeit. Kryst. Min.*, 13, 623—624, from *Tschermak's min. Mitth.*, 7, 455—458; 8, 190).—In 1883, beryl was discovered in mica-schist, on the north side of the Ifinger, near Meran. The crystals are sometimes as much as 18 cm. long and 34 cm. in circumference. Analysis gave the following results:—

SiO_2.	Al_2O_3.	BeO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
66·49	23·01	9·30	0·54	0·54	0·04	99·92	2·69

B. H. B.

Micas of the Pegmatite-Granite of Schüttenhofen. By R. Scharizer (*Zeit. Kryst. Min.*, 13, 449—473).—At Schüttenhofen, a deposit of pegmatite-granite occurs intercalated in magnesian limestone. The minerals, 18 in number, forming this rock separate into three typical associations or zones. Only one mineral, grey quartz, occurs in all three zones. The first zone, which forms the principal portion of the pegmatite deposit, consists of microcline, lepidomelane, and silver-white to tombac-brown muscovite, with the phosphates apatite, monazite, and xenotime. The second zone is formed of white albite, yellowish-white muscovite, bluish-black tourmaline, and brown manganese-garnet, with small quantities of light-green tourmaline. In the third zone appear typical lithium minerals: blood-red lepidolite, dark-green and pink tourmaline, with bluish-white albite (clevelandite). The variously coloured micas gave on analysis the results given in the accompanying table:—

	I.	II.	III.	IV.
SiO_2	35·30	43·67	44·08	49·26
TiO_2	1·20	—	—	—
SnO_2	0·16	—	—	0·06
Al_2O_3	22·62	36·69	36·84	25·26
Fe_2O_3	5·68	2·10	0·48	—
FeO	18·04	0·55	0·74	0·84
MnO	1·19	trace	0·25	0·85
MgO	3·69	—	CaO = 0·21	—
$(K,Rb,Cs)_2O$	8·60	8·57	11·10	13·85
Na_2O	0·62	1·95	0·20	0·35
Li_2O	0·30	trace	0·37	5·38
H_2O	1·21	4·35	4·98	1·76
Aq	2·30	1·15	1·17	—
F	0·60	0·35	0·19	5·68
Total	101·51	99·38	100·61	103·29
Less O	0·25	0·14	0·08	2·38
Total	101·26	99·24	100·53	100·91

I. Black lepidomelane; sp. gr. 3·0826; formula, $H_2R'_4R''_6R'''_8Si_{10}O_{41}$. II. Tombac-brown muscovite from the first zone; sp. gr. 2·8349; formula almost exactly that of damourite. III. Yellowish-white muscovite from the second zone; sp. gr. 2·8540. This analysis is in accord with that of the muscovite of Auburn, given by Clarke (Abstr., 1887, 347). IV. Lithionite from the third zone; sp. gr. 2·8245; formula, $(HO,F)_6R'_8Al_6Si_{10}O_{30}$. This formula differs from that given by Clarke and by Groth, in that the author's formula presents an excess of R'_2SiO_3. A consideration of the various recent analyses of lepidolite indicates that the lithium micas form a continuous series, the members of which may be regarded as isomorphic mixtures of two terminal members. The author suggests that these terminal members are the pure muscovite silicate $R'_6Al_6Si_6O_{24}$, and the silicate

$$(HO,F)_6R'_8Al_6Si_{10}O_{30},$$

for which the name lithionite silicate is proposed. In the analyses given, the substance was dried at 100°, and in calculating the formula the water given off at 300°, indicated as Aq, was disregarded.

B. H. B.

Schorlomite, a Variety of Melanite. By G. A. König (*Zeit. Kryst. Min.*, **13**, 650, from *Proc. Acad. Nat. Sc. Philad.*, 1886, 355).—Melanite, from California, containing titanium, and occurring as black masses in a greenish-yellow matrix, gave on analysis the following results (I):—

	SiO_2.	TiO_2.	Ti_2O_3.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	CO_2.	MnO.	Total.
I.	30·71	4·47	3·29	2·26	22·67	32·41	0·30	3·36	—	99·47
II.	25·80	12·46	4·44	1·00	23·20	31·40	1·22	—	0·46	99·98

For comparison, the results (II) are given of an analysis of black schorlomite from Magnet Cove, Arkansas. The ratio of the constituents of the melanite (I) and of the schorlomite (II) is:—

$(SiTi)O_2$	:	$(FeTiAl)_2O_3$	:	$(CaMgMn)O$.	
3·03	:	1	:	3·10	(I)
3·16	:	1	:	3·22	(II)

These results appear to support the theory that schorlomite is a garnet in which titanium, in the form of Ti_2O_3, is substituted for aluminium.

B. H. B.

Tin-ore Deposits of Mount Bischoff. By A. v. Groddeck (*Zeit. Kryst. Min.*, **13**, 636, from *Zeit. deutsch. geol. Ges.*, **38**, 370).—The author comes to the conclusion that, like the topaz rock of the Schneckenstein in Saxony, the rock of the tin-ore district of Mount Bischoff in Tasmania is a quartz porphyry converted into topaz. This alteration probably occurred during the formation of the tin-ore deposits. This theory is supported by the discovery of pseudomorphs of topaz after quartz. The interior of the crystals consisted of colourless quartz, whilst the exterior consisted of a dull white massive envelope of topaz, which gave on analysis the following results:—

SiO_2.	Al_2O_3.	F.	CaO.	SnO_2.	Total.
56·32	35·91	10·68	0·03	2·42	105·36

or, in other words, 63·21 per cent. of topaz, 35·39 per cent. of quartz, and 2·42 per cent. of tin oxide (compare Abstr., 1886, 603).

B. H. B.

Volcanic Blocks of Monte Somma. By B. Mierisch (*Zeit. Kryst. Min.*, **13**, 627—628, from *Tschermak's min. Mitth.*, **8**, 113).—In the cavities of blocks of altered limestone, the author found grains of a colourless mineral hitherto supposed to be quartz. Analysis gave the following results:—

SiO_2.	MgO.	FeO.	Na_2O.	K_2O.	Ignition.	Total.
41·85	56·17	1·07	0·12	0·40	0·19	99·80

The mineral is obviously forsterite. It occurs in association with spinell and calcite. The occurrence of a silicate free from lime in a limestone block is remarkable.

In silicate blocks, especially in one composed principally of augite and melilite, the author found a colourless mineral occurring in thin acicular crystals. It belongs to the nepheline group. It is optically monaxial, negative, exhibits basal cleavage, is very brittle, and has a sp. gr. of 2·602. Analysis gave the following results :—

SiO_2.	$Al_2O_3 + Fe_2O_3$.	CaO.	K_2O.	Na_2O.	Total.
37·44	32·43	2·18	27·20	2·26	101·51

The mineral is thus a potassium-nepheline, $K_2Al_2Si_2O_8$, for which the author proposes the name of *kaliophilite*. B. H. B.

Selenium in Meteoric Iron. By H. N. Warren (*Chem. News*, **57**, 16).—Results are given below of the analysis of specimens of meteoric iron: 1 and 2 from Bohumilitz; 3, Pallus iron; 4, Elbogen; 5 and 6, Atacama Desert. In the method employed, 10 grams of the roughly-powdered specimen is mixed with sufficient flowers of sulphur, and heated to redness in a tube in a current of oxygen, the products of combustion passing into a series of bulbs containing distilled water, where the selenious acid is reduced by the sulphurous acid. The solution with the selenium precipitate is heated at 27°, and ultimately the latter is dried in an air-bath and weighed. In each case, a blank experiment was made with the sulphur employed.

	1.	2.	3.	4.	5.	6.
Fe	90·10	94·51	95·04	88·20	70·01	86·52
Ni	6·54	2·54	3·20	8·20	20·02	10·52
Mn....	0·12	—	0·12	0·23	—	—
Co	0·24	0·32	0·12	0·12	—	0·12
Cu	—	—	0·20	—	—	—
Se	0·23	0·05	0·04	0·06	0·08	0·05

D. A. L.

Water from the Tönnissteiner Medicinal Spring. By B. Lepsius (*Ber.*, **21**, 552—556).—This water contains a large excess of carbonic acid, and has an alkaline chalybeate taste; on analysis, the following results were obtained, which, when compared with a

Grams per litre.	1887. Lepsius.	1868. Fresenius.	Grams per litre.	1887. Lepsius.	1868. Fresenius.
K_2SO_4	0·07213	0·09900	$CaCO_3$	0·28072	0·38275
Na_2SO_4	0·15324	0·14763	$MgCO_3$..........	0·79622	1·07426
NaI	0·00004	0·00001	$FeCO_3$	0·02908	0·02138
NaCl	1·40236	1·41489	$MnCO_3$..........	0·00015	0·00031
NaBr	0·00064	0·00080	SiO_2	0·02461	0·02741
$NaNO_3$	0·00071	0·00046	B_2O_3	trace	trace
Na_2HPO_4	0·00003	0·00018	NaF	„	„
$Al_2(PO_4)_3$	0·00017	0·00013			
Li_2CO_3	0·00303	0·00390	Total solids	4·51335	4·99855
Na_2CO_3	1·74564	1·81999	CO_2 half combined	1·30119	1·49961
$(NH_4)_2CO_3$	0·00452	0·00533	CO_2 free	2·79929	2·39334
$BaCO_3$	0·00001	0·00006			
$SrCO_3$	0·00005	0·00006	Total	8·61383	8·89150

former analysis by Fresenius, show that the composition has remained practically unaltered for the last 20 years. F. S. K.

Organic Chemistry.

Decomposition of Petroleum by Heat. By K. LISSENKO (*Dingl. polyt. J.*, **266**, 226, from *J. Berg u. Huttenwesen*, 1887, 349).—When petroleum is subjected to distillation, it is not only split up into constituents having different boiling points, but the high boiling products are decomposed into those of a lower boiling point. The yield of the latter increases with the time of heating, and in this manner the quantity of kerosine from Caucasian petroleum, which usually does not exceed 30 per cent., may be doubled. The best yield of kerosene is obtained from petroleum residues at a temperature of 434° to 501°. Nobel, however, found that the decomposition of the residues is best effected at 400°. D. B.

Action of Bromine on Iodoform. By K. LÖSCHER (*Ber.*, **21**, 410).—By the action of bromine on iodoform, bromoform alone is obtained, and this, whether the bromine is employed in small quantity or in excess. The substance described by Serullas (*Ann. Chim. Phys.* [2], **34**, 225, and **39**, 97), and by Bouchardat (*Annalen*, **22**, 233) as bromiodoform, is merely a solution of iodoform in bromoform. A. J. G.

Action of Zinc Ethyl on Nitroethane. By J. KISSEL (*J. Russ. Chem. Soc.*, 1887, 109—113).—In order to test the accuracy of the view he formerly expressed, that nitroethane is a compound of the constitution $CH_3 \cdot CO \cdot NH \cdot OH$ (Abstr., 1885, 364), the author has studied the action of zinc ethyl on nitroethane. After several days' action at 0° in a sealed tube the mixture becomes solid, and when the tube is opened an inflammable mixture of gases escapes which is free from ethylene. The contents of the tube consist of a mixture of two compounds at least, of which one is crystalline and the other amorphous. The crystalline compound is decomposed by water containing a little sulphuric acid, and the nitroethane removed by evaporation, the liquid neutralised, and the zinc precipitated by sodium carbonate; on adding potash and distilling, a liquid boiling at 126—133° passes over. On neutralising this with hydrochloric acid, it yields the hydrochloride of a substituted hydroxylamine, $NHEt_2O,HCl$. Another compound of similar composition is found among the numerous products formed in the reaction. B. B.

Isobutylene Bromide and Bromotrimethyl Carbinol. By I. GUARESCHI and L. GARZINO (*Chem. Centr.*, 1887, 1343—1344, from *Ann. Chim. Farm.*, **87**, 101—112).—The moderately stable *barium isobutylenedisulphonate*, $C_4H_8(SO_3)Ba + 2H_2O$, was prepared by boiling 25 grams of isobutylene bromide with a saturated solution of ammonium sulphite for 9 to 12 hours, then boiling with an excess of baryta-water, precipitating the uncombined barium with carbonic anhydride, and treating the concentrated filtrate with 95 per cent. alcohol. The free acid has not been crystallised. If the filtrate from this barium salt is evaporated to drive off the alcohol, and again treated with absolute alcohol, *barium γ-hydroxyisobutylenesulphonate*, $(OH{\cdot}C_4H_8{\cdot}SO_3)_2Ba + 1\frac{1}{2}H_2O$, and barium chloride separate. The formula $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}SO_3H$, has been given to the acid. The alcoholic filtrate from the last barium salt contains still another salt containing the same amount of barium. Isobutaldehyde is also formed by this reaction. If 30 grams of bromotrimethylmethane, CMe_3Br, is boiled with 150 c.c. of a saturated solution of ammonium sulphite, an inflammable gas (isobutylene?), trimethyl carbinol, boiling at 80·5° to 81·5°, and trimethylmethanesulphonic acid are produced. By simply boiling the bromide with 3 parts of water, isobutane and trimethyl carbinol are formed.

When bromo-γ-isobutane is boiled for five hours with 5 parts of water, isobutaldehyde and *monobromotrimethyl carbinol*, $CH_2Br{\cdot}CMe_2{\cdot}OH$, are formed. The latter is a liquid boiling at 138—140°, of sp. gr. 1·429 at 0°, insoluble in water, but soluble in ether. J. P. L.

Compounds of Sodium Hydroxide and Methyl Alcohol. By C. Göttig (*Ber.*, **21**, 561—565).—When a methyl alcohol solution of soda is evaporated to a certain consistency, it solidifies to a crystalline mass on cooling; this compound, after drying, behaves similarly to those obtained from ethyl alcohol and soda or potash; namely, when agitated with water or some other liquids, it moves about on the surface, decomposes, and dissolves.

The composition of the compound formed varies with the conditions of its formation. (1.) If anhydrous methyl alcohol is employed and all moisture carefully excluded, the composition of the substance formed is $5NaOH,6MeOH$, when crystallisation is allowed to proceed slowly. (2.) When a little water is present, the composition is $NaOH,\frac{1}{2}H_2O,MeOH$. (3.) The composition varies when a considerable quantity of water is present, and seems to depend chiefly on the specific gravity of the solidifying solution, and on the relation between the quantities of water and alcohol.

Methyl alcohol also forms compounds with potash, and many other alcohols combine with potash and soda in a similar manner.

F. S. K.

Specific Gravities of Aqueous Glycerol Solutions. By W. W. J. Nicol (*Pharm. J. Trans.* [3], **18**, 302).—The following are determinations of the specific gravity at 20° of definite mixtures of glycerol and water:

Glycerol per cent.	Specific gravity.
100	1·26348
90	1·23720
80	1·21010
70	1·18293
60	1·15561
50	1·12831
40	1·10118
30	1·07469
20	1·04884
10	1·02391
Water at 20°	1·00000

A table calculated from these results for intermediate percentages is given in the paper. R. R.

Action of Boiling Acids on Methylenitan. By C. Wehmer and B. Tollens (*Annalen*, **243**, 334—342).—The authors maintain that the so-called formose which Loew obtained (this vol., p. 245) by the action of lime on formaldehyde is not a true carbohydrate, as it does not yield levulinic acid when heated with hydrochloric or sulphuric acid. W. C. W.

Levulose. By H. Winter (*Chem. Centr.*, 1887, 1373—1374, from *Zeit. Rüb. Zuck. Ind.*, **24**, 796—820).—The specific rotatory power of a 20 per cent. solution of levulose is −71·4 at 20°. The discrepancies between the old and new values for the specific rotatory power of levulose cannot be attributed to the manner or source of production, inasmuch as they are found to have no influence.

Alcohol diminishes the rotatory power of levulose in a marked degree, but increases that of dextrose; the former phenomenon may probably be accounted for by the fact that levulose forms an alcoholate of the formula $C_6H_{11}EtO_6$. The specific rotatory power of anhydrous levulose in absolute alcohol is −47° for a concentration of 7·78 per cent.

As a mixture of equal parts of levulose and dextrose does not exhibit the optical properties of invert sugar, it is possible that the latter consists of four parts of levulose to three of dextrose. Levulose and dextrose in the proportion of two parts of the former to one of the latter form a well-defined crystalline product, which in solution exhibits no trace of birotation similar to that which exists in the case of a mechanical mixture in the same proportions. On account of the existence of this compound, a complete separation of the two sugars by means of alcohol is impossible.

An acetyl compound of levulose could not be obtained. Compounds of levulose with lime, lead oxide, chloride, and nitrate, iron and bismuth nitrate, were obtained. J. P. L.

Irisin. By O. Wallach (*Ber.*, **21**, 396—397).—Ekstrand and Johanson recently described a carbohydrate from *Phleum pratense*, to which they gave the name of graminin (see this vol., p. 246, also next Abstract). In the author's opinion, this is identical with irisin, the carbohydrate from *Iris pseudacorus* (Abstr., 1887, 526).

A. J. G.

Carbohydrates. By Å. G. EKSTRAND and C. J. JOHANSON (*Ber.*, **21**, 594—597).—The authors have found it necessary to modify some of the statements made in their last paper (this vol., p. 246), as it is now shown that they had confounded two carbohydrates under the name of graminin. To that which occurs in the haulm of *Phleum pratense*, and, mixed with another, in the rhizome of *Baldingera*, they give the name of *phlein*, reserving the name of graminin for a carbohydrate occurring much more widely diffused in the Gramінaceæ.

Graminin, $6C_6H_{10}O_5 + H_2O$, occurs in the rhizomes of *Trisetum alpestre*, *Agrostis*, *Calamagrostis*, *Festuca*, *Avena*, and in certain parts of *Baldingera*. It is lævorotatory; $[\alpha]_D = -38\cdot89$; 100 parts of an aqueous solution at 9—10° contain 22·80 parts of graminin (dried at 100°); the sp. gr. of graminin dried at 100° is 1·522; it melts at 209°, and forms doubly refracting sphærocrystals.

Phlein: $[\alpha]_D = -48\cdot12$ to $-48\cdot91$; sp. gr. = 1·480; melting point 215°; 100 parts of the aqueous solution contain 3·26 parts of phlein (dried at 100°).

A. J. G.

Ethylamine-derivatives. By S. GABRIEL (*Ber.*, **21**, 566—575).—It has been found that bromethylphthalimide can be prepared by a more convenient method than that already described (Abstr., 1887, 1037), as the reaction between potassium phthalimide and ethylene bromide takes place considerably below 200°, and can be carried out in open vessels. This method is described in detail.

β-Bromethylamine hydrobromide, $C_2H_4Br{\cdot}NH_2,HBr$, is obtained by heating bromethylphthalimide with concentrated hydrobromic acid for two hours at 180—200° in sealed tubes. The product crystallises from alcohol in rhombic forms and melts at 155—160°; it is readily soluble in water, and when treated with concentrated potash yields an oil containing free bromethylamine. The *picrate*,

$$C_2H_4Br{\cdot}NH_2,C_6H_2(NO_2)_3{\cdot}OH + \tfrac{1}{2}H_2O,$$

crystallises in amber-yellow prisms or needles which melt when placed in a capillary tube in boiling water, and gradually solidify again; the anhydrous salt melts at 130—131·5°. The *platinochloride*, which is tolerably soluble in water, forms orange-yellow scales.

When an aqueous solution of bromethylamine hydrobromide is boiled with silver carbonate, a product is obtained which crystallises from alcohol in flat, transparent forms, melts at 90—91°, and dissolves in water without alkaline reaction. This compound has the formula $C_3H_5NO_2$, and may be regarded as the anhydride of hydroxyethylcarbamic acid, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}COOH$.

Bromethylphthalimide is decomposed by heating with sulphuric acid (1 pt. acid, 2 pts. H_2O); the filtrate from the phthalic acid yields three products. (1.) When the filtrate is freed from hydrobromic acid and sulphuric acid and evaporated, a syrup is obtained, from which the addition of a considerable quantity of a 1 per cent. solution of picric acid precipitates a yellow, microcrystalline powder. This substance softens at 200° and melts at 205—210°. The mother-liquor yields on further evaporation slender, yellow, crystalline needles of *hydroxyethylamine picrate*, $OH·C_2H_4·NH_2,C_6H_3N_3O_7$, which after recrystallisation from alcohol melts at 159·5°. (2.) If the filtrate is freed from sulphuric acid by adding barium carbonate and the excess of carbonate removed by careful addition of dilute sulphuric acid, a yellow, crystalline, hygroscopic mass is obtained on evaporation. This compound is *β-hydroxyethylamine hydrobromide*, $OH·C_2H_4·NH_2,HBr$; it crystallises in needles which melt below 100°, and its alcoholic solution gives with platinum chloride an oily platinochloride which gradually becomes crystalline and is very soluble in water.

A very soluble acid compound is formed when bromethylphthalimide is treated with warm potash; after neutralising the free alkali with hydrochloric acid and evaporating the solution, a residue is obtained which, when heated at 130—150° for about half an hour, is converted into *β-hydroxyethylphthalimide*, $C_8H_4O_2N·C_2H_4·OH$; this substance is only sparingly soluble, and crystallises from water in colourless needles or rhombic leaves; it melts at 126—127° and is soluble in alcohol; it is insoluble in ammonia but gradually dissolves in potash.

The very soluble compound referred to above is probably *hydroxyethylphthalamic acid*; the *hydrochloride*,

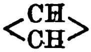
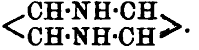
$$COOH·C_6H_4·CO·NH·C_2H_4·OH,HCl,$$

was obtained in the form of colourless crystals melting at 85·5°. It dissolves in water, yielding an acid solution from which silver nitrate precipitates silver chloride. When boiled with silver carbonate, a colourless syrup is obtained which, on distillation, gives hydroxyethylphthalimide and water; the former distils above 360°, apparently not without decomposition, the crystalline distillate melting at 124—125°, and after crystallising from water at 126—127°. *β-Chlorethylamine hydrochloride*, $C_2H_4Cl·NH_2,HCl$, is formed when oxyethylphthalimide is heated with concentrated hydrochloric acid for three hours at 180—200°. On account of the extreme solubility of this salt in water, alcohol, and alcoholic ether, it could not be purified, but the *picrate*, $C_2H_4Cl·NH_2,C_6H_3N_3O_7 + \frac{1}{2}H_2O$, was prepared. This salt crystallises in long, yellow needles, which lose water of crystallisation at 100°, and on heating quickly melt slightly above 100°. The anhydrous compound melts at 142—143°. The *platinochloride* crystallises in orange-coloured, microscopic, hexagonal plates, which dissolve readily in water, but only sparingly in alcohol or concentrated hydrochloric acid.

Chlorethylamine hydrochloride, when treated with potash, behaves in a manner similar to bromethylamine hydrobromide, but the free base seems to be more stable than the corresponding bromine-derivative.

Ethylene chloride acts on potassium phthalimide only at a much higher temperature than the bromide, and yields chiefly ethylenediphthalimide. Ethylene chlorobromide and potassium phthalimide give a product consisting of chlorethyl- and bromethyl-phthalimide and ethylenediphthalimide; the mixture of the two haloïd compounds melts at 81—83°. F. S. K.

Ethylenimine (Spermine). By A. LADENBURG and J. ABEL (*Ber.*, **21**, 758—766).—When heated, ethylenediamine hydrochloride is partially converted into ethylenimine hydrochloride, the reaction being best effected by heating portions of 3 to 5 grams in small glass bulbs. The heating is stopped as soon as the contents have sublimed into the upper part of the bulb. The brown, carbonaceous mass is extracted with water, filtered, and the filtrate treated with a solution of potassio-bismuth iodide; the crystalline precipitate of the bismutho-iodide is then separated from an amorphous precipitate that falls at the same time. The yield is very small, the temperature at which ethylenediamine hydrochloride is converted into ethylenimine hydrochloride being above that at which the latter salt begins to decompose.

Ethylenimine,  $<\!\begin{smallmatrix}CH\\CH\end{smallmatrix}\!>NH$?, is prepared by distilling the bismutho-iodide with potash, evaporating on the water-bath, and drying under an exsiccator. The product so obtained, however, is not a base of low boiling point, as was expected, but a white, porcelain-like mass which deliquesces on exposure to air with absorption of water and carbonic anhydride. It melts at 159—163° in sealed tubes, can be sublimed, is insoluble in ether, readily soluble in absolute alcohol. The vapour-density is 2·93, corresponding with the doubled-molecular formula  $<\!\begin{smallmatrix}CH{\cdot}NH{\cdot}CH\\CH{\cdot}NH{\cdot}CH\end{smallmatrix}\!>$. There seems some reason to think that the original distillate contains the base with the simple formula; it has a faint, piperidine-like odour which soon disappears, even when kept in closed vessels, and the readiness with which the base had passed over with the steam would seem to point in the same direction.

The *hydrochloride*, C_2H_5N,HCl, crystallises in transparent tables, readily soluble in water, insoluble in alcohol. The *platinochloride*, $(C_2H_5N)_2,H_2PtCl_6$, forms small, well-formed, yellow prisms. The *aurochloride* crystallises in yellow, nacreous plates. The *picrate* forms small tables. The *mercurochloride* crystallises in feathery groups of needles. The *bismutho-iodide*, $3C_2H_5NHI,2BiI_3$, crystallises in lustrous, garnet-red plates, insoluble in cold, decomposed by boiling water.

Although the evidence is not yet absolutely conclusive, there seems strong reason to think that ethylenimine is identical with the base, spermine, obtained by Schreiner from human semen (Abstr., 1879, 72). This point is still under investigation. A. J. G.

Action of Hydrogen Phosphide on Aldehydes and Ketonic Acids. By J. MESSINGER and C. ENGELS (*Ber.*, **21**, 326—336).—A slow, constant current of hydrogen phosphide can readily be obtained from phosphonium iodide by suspending it in ether (which must not be too moist for this purpose), and adding a few drops of water from time to time as the rate of evolution of the gas diminishes; 5 grams of the iodide will in this way furnish a regular supply of gas for about an hour. It is best to work with small quantities of the iodide, and to add more as required. The gas is perfectly pure and free from iodine, is not spontaneously inflammable, and does not seem to be poisonous. The hydrogen iodide formed by the decomposition of the phosphonium iodide is wholly retained by the ether with the formation of a heavy, colourless oil which is insoluble in ether, has the composition $(Et_2O)_2HI$, is decomposed by water with the formation of ether, hydriodic acid, and ethyl iodide, and on distillation yields first ether, then ethyl iodide, and finally hydriodic acid of the composition $2HI + 11H_2O$, boiling at 125°. Ether also forms a corresponding additive compound on treatment with hydrogen bromide.

No absorption of the gas occurs under any conditions when a current of hydrogen phosphide alone is led through an aldehyde, but if at the same time hydrogen chloride is also passed through absorption takes place and is rendered more complete by adding ether to the aldehyde. The following compounds have been obtained from the corresponding aldehydes under these conditions.

Tetrahydroxyethylidenephosphonium chloride, $P(CHMe{\cdot}OH)_4Cl$, crystallises in quadratic forms, melts at 112°, and is readily soluble in alcohol, insoluble in ether and carbon bisulphide. It has an unpleasant odour, is decomposed by water, and on treatment with aqueous potash is converted into Girard's tetrahydroxyethylidenephosphine and its hydroxide (Abstr., 1884, 1119). In addition to the chloride, an oil is also obtained, particularly when an excess of hydrogen chloride is passed into acetaldehyde, which seems to have the composition $[(COHMe)_2HCl]_3PH_3$; it is readily soluble in alcohol, insoluble in ether, and decomposes on distillation. The corresponding bromine-derivatives were prepared by passing a current of hydrogen bromide together with hydrogen phosphide through acetaldehyde. The *bromide*, $P(CHMe{\cdot}OH)_4Br$, crystallises in quadratic forms, melts at 88°, and deliquesces on exposure to the air. The oil, which is formed simultaneously, has the composition $[(COHMe)_3HBr]_3PH_3$.

Tetrahydroxypropylidenephosphonium chloride, $P(CHEt{\cdot}OH)_4Cl$, is crystalline, melts at 128°, and is readily soluble in alcohol, sparingly soluble in carbon bisulphide and chloroform, and insoluble in ether. It has an unpleasant, persistent odour, and is decomposed by water. The *bromide*, $P(CHEt{\cdot}OH)_4Br$, crystallises in slender needles, melts at 105—106°, and closely resembles the chloride.

Isobutaldehyde and acraldehyde also absorb the gases, but the products were not obtained in the crystalline condition.

Benzaldehyde, under like conditions, yields a compound,

$$(COHPh)_4,PH_3,$$

which crystallises in slender needles, melts at 153°, and is readily soluble in hot alcohol and chloroform, sparingly soluble in hot water, and insoluble in benzene, light petroleum, and carbon bisulphide. Metanitrobenzaldehyde forms an analogous compound,

$$(NO_2{\cdot}C_6H_4{\cdot}COH)_4PH_3;$$

cinnamaldehyde, under similar conditions, yields a crystalline compound, which, however, is not homogeneous; salicylaldehyde does not form a crystallisable derivative.

When an ethereal solution of pyruvic acid is simultaneously treated with hydrogen phosphide and a rapid current of hydrogen chloride, a compound, $C_9H_9O_6P$, is obtained which crystallises in slender, silky needles, sublimes without melting, and is insoluble in ether, alcohol, chloroform, carbon bisulphide, and light petroleum, but readily soluble in ammonia and aqueous soda.

Acetone, ethyl acetate, and ethyl oxalate do not seem to react with hydrogen phosphide. The research is being continued.

W. P. W.

Amidoacetals. By A. Wohl (*Ber.*, **21**, 616—618).—*Amidoacetal*, $CH(OEt)_2{\cdot}CH_2{\cdot}NH_2$, is prepared by heating chloracetal with alcoholic ammonia for 14 hours at 150—160°; the product is then mixed with sufficient baryta to decompose the chlorides, heated as long as ammonia comes off, and finally distilled with steam, when the primary base alone passes over. It is a colourless oil which shows the characteristic reactions both of a primary amine and an acetal. The *hydrochloride* is crystalline, very hygroscopic, and readily soluble in alcohol and alcohol-ether; the *platinochloride*, $(C_6H_{15}NO_2)_2,H_2PtCl_6$, crystallises in hexagonal forms. When an aqueous solution of the base is treated with excess of dilute sulphuric acid, and the liquid, after being made alkaline, is distilled with steam, a volatile base passes over; the aqueous solution of this base loses its alkalinity after a time, and on evaporation leaves a solid residue. Whether these substances are amidoaldehyde and the corresponding ketine will appear on further investigation.

An amido-compound is also obtained by the action of alcoholic ammonia on β-chloropropionacetal. A. J. G.

Conversion of Ketoximes into Pseudonitroles. By R. Scholl (*Ber.*, **21**, 506—510).—Acetoxime (1 part) dissolved in ether (20 parts) is treated with rather less than the calculated amount of nitrogen peroxide, and the whole left until it has a deep blue colour and gives off no more gas. The product is washed with aqueous soda solution, then with water, dried with calcium chloride, and evaporated in a vacuum. Colourless crystals of propylpseudonitrole, $NO{\cdot}CMe_2{\cdot}NO_2$, remain. The reaction seems to be capable of general application. Butylpseudonitrole was prepared from methylethylketoxime.

Diethylketoxime, $CEt_2N{\cdot}OH$, is prepared by boiling diethylketone with a solution of hydroxylamine hydrochloride and soda in presence of alcohol for one to two hours; it is a colourless oil, boils at 162—163° under 726 mm. pressure, and is insoluble in water.

Amylpseudonitrole, $NO{\cdot}CEt_2{\cdot}NO_2$, obtained as above from diethylketoxime, forms large, tabular crystals, melting at 63°, and is soluble, with blue colour, in ether and chloroform.

An impure octylpseudonitrole is obtained in like manner from methylhexylketoxime. The latter boils at 213—214°.

N. H. M.

Tetrachlorinated Diacetyl. By S. Levy and K. Jedlička (*Ber.*, **21**, 318—321).—Experiments made by the authors show that the oily product obtained by Stenhouse (this Journal, 1870, p. 8) by the action of chlorine in the presence of iodine on chloranilic acid is pentachloracetone.

When chloranilic acid is treated with potassium chlorate and hydrochloric acid, noteworthy quantities of oxalic acid are formed together with a neutral brownish-yellow liquid which distils with partial decomposition at 180—196°. The distillate is a yellow oil, and consists of two substances, one of which (the chief product) is liquid, and the other a crystalline solid; the latter can be separated by crystallisation in a freezing mixture, and forms beautiful, yellow scales. The liquid product is purified by addition of water, which converts it into the crystalline *hydrate* of *symmetrical tetrachloracetone*, $CHCl_2{\cdot}CO{\cdot}CHCl_2 + 4H_2O$. This crystallises from water in colourless, long prisms, melts at 48—49°, loses its water of crystallisation on further heating, and boils at 179—181° at 725 mm. pressure.

The coloured crystalline product is most probably *symmetrical tetrachloracetyl*, $CHCl_2{\cdot}CO{\cdot}CO{\cdot}CHCl_2$. It crystallises from ether in large, yellow tables, melts at 83—84°, and boils at 201—203° with slight decomposition at 740 mm. pressure yielding a yellowish-green vapour. It has a pungent odour, is soluble in water, alcohol, and ether, and is turned brown on treatment with aqueous soda and ammonia. Ammoniacal silver solution is not reduced by it, and no trace of red colour can be detected when it is added to a magenta solution decolorised by sulphurous anhydride. Finally, when treated with phenylhydrazine, it yields a very characteristic *phenylhydrazide*, which crystallises in slender, orange-red, woolly needles, melts at 186° with decomposition, and is very sparingly soluble in alcohol. The research is being continued. W. P. W.

Thiocarbonyl Chloride. By H. BERGREEN (*Ber.*, **21**, 337—352). —The decomposition of thiocarbonyl chloride by water, which takes place very slowly in the cold, is complete at the end of a few hours on boiling. The products of the reaction are carbonic anhydride, hydrogen sulphide, and hydrogen chloride.

When dissolved in anhydrous ether free from alcohol, and saturated with carefully dried ammonia, thiocarbonyl chloride is converted into ammonium thiocyanate (compare Rathke, *Annalen*, **167**, 195), ammonium chloride, and a third substance which, however, could not be identified owing to the small quantity obtained. The thiamidoformic chloride, $CSCl{\cdot}NH_2$, which might possibly be regarded as an intermediate product of this reaction, was not formed by heating the chloride with ammonium chloride at 200° for some hours; on the contrary, complete decomposition occurred with the formation of carbon bisulphide and carbon tetrachloride. This result is due in some way to the presence of ammonium chloride, since thiocarbonyl chloride is decomposed only to a very slight extent when heated alone at 200° for a similar period.

Diphenylamine reacts with thiocarbonyl chloride in ethereal solution to form a compound which crystallises in small, pale-yellow needles, melts at 196°, and is probably identical with Bernthsen and Friese's tetraphenylthiocarbamide (Abstr., 1882, 1089).

When thiocarbonyl chloride (5 grams), dissolved in benzene free from thiophen (25 grams), is treated with powdered aluminium chloride (8 to 10 grams) and the mixture heated on a water-bath for some time until hydrogen chloride ceases to be evolved, a compound is obtained whose composition approximates to that required for *thiobenzophenone*, $CSPh_2$. This is a reddish-brown oil which dissolves readily in ether, benzene, and hot alcohol, and decomposes on distillation yielding a crystallisable distillate free from sulphur. When treated with hydroxylamine or with phenylhydrazine, it gives off hydrogen sulphide, and is converted into diphenylacetoxime or the phenylhydrazide of benzophenone respectively; hence it must be regarded as a thioketone. Behr (this Journal, 1873, 276) and Engler (Abstr., 1879, 61) have obtained compounds containing sulphur which have been described as thiobenzophenone; these substances, however, do not react either with hydroxylamine or phenylhydrazine, and cannot, therefore, be thioketones. The author suggests that Engler's compound (m. p. = 146·5°) may be a polymeride of thiobenzophenone corresponding with Wislicenus' thioduploacetone. Thiocarbonyl chloride also reacts with zinc methyl and zinc ethyl, and the compound obtained from the latter is a pungent, red oil, which can be distilled with steam. On analysis it was found to contain only four-fifths the amount of sulphur required for the formula $CSEt_2$, and the non-crystallisable oil obtained, together with hydrogen sulphide, on treating its alcoholic solution with phenylhydrazine, yielded only one-half the nitrogen required for the formula $CEt_2{:}N_2PhH$; these results are, however, attributed to the difficulty of purifying the compound, which most probably is *diethylthioketone.*

Ethyl chlorothioformate is obtained by the action of thiocarbonyl chloride (1 mol.) on an alcoholic solution of sodium ethoxide (1 mol.). The boiling point of this compound is probably 130—135°, but the specimen obtained boiled at 130—160°; its identity was, however, established by its conversion into xanthogenamide on treatment with aqueous ammonia. When 2 mols. of sodium ethoxide are employed, ethyl thiocarbonate is obtained (compare Klason, Abstr., 1887, 1029). The reaction with a solution of phenol in aqueous soda results in the formation of phenyl thiocarbonate, $CS(OPh)_2$, which forms white, lustrous crystals, and melts at 97°.

The action of thiocarbonyl chloride on ketonic derivatives of the type of ethyl acetoacetate results in the displacement of both the hydrogen-atoms of the methylene-group by the thiocarbonyl radicle. Ethyl thiocarbonylacetoacetate $(CS{:}CAc{\cdot}COOEt)_x$ (compare Norton and Oppenheim, *Ber.*, **10**, 703), for example, is obtained from ethyl sodacetoacetate and from ethyl cupracetoacetate; this compound does not react with phenylhydrazine or hydroxylamine, and probably is not a thioketone. An oil which could neither be crystallised nor distilled, and which contained sulphur but not chlorine, was formed when ethyl sodiomethacetoacetate in ethereal solution was treated with the chloride. Under like conditions, ethyl sodiomalonate yields the *thiocarbonyl*-derivative $CS{:}C(COOEt)_2$, which crystallises in small, flesh-coloured needles, and melts at 177—178°. When this compound is saponified with alcoholic potash, and the product dissolved in water and treated with dilute sulphuric acid, hydrogen sulphide is evolved in small quantity, and a crystalline acid is obtained which cannot be recrystallised, since it decomposes partially on solution with the evolution of hydrogen sulphide. The analytical results are consequently only approximate, but they point to the formulæ $CS\colon C(COOH)_2$ for the acid, and $CS\colon C(COOAg)_2$, for the *silver* salt; the latter is pale-yellow in colour, and when touched with a small flame explodes like gunpowder, with the formation of silver sulphide, carbonic anhydride, and carbon. Thiocarbonyl chloride and ethyl sodiobenzoylacetate also react, forming *ethyl thiocarbonylbenzoylacetate*, $(CS\colon CBz{\cdot}COOEt)_x$, which crystallises in yellowish needles, melts at 162—164°, and dissolves in sulphuric acid with a yellow colour. Lastly, the sodium compound of desoxybenzoïn is converted, under similar conditions, into the *thiocarbonyl*-derivative, $C_{15}H_{10}OS$, which crystallises in small, golden-yellow needles, melts at 285—286°, is much more sparingly soluble in ether, carbon bisulphide, light petroleum, and hot alcohol than the thiocarbonyl-derivatives of ethyl acetoacetate and ethyl malonate, and dissolves in concentrated sulphuric acid with a deep bluish-violet colour, recalling that of permanganate in solution. W. P. W

Calcium Copper Acetate. By F. RÜDORFF (*Ber.*, **21**, 279—281).—Calcium copper acetate, which was first prepared by Brewster (*Schweigger's Jahresb.*, **33**, 342), does not contain 8 mols. of H_2O, but has the composition $Ca(C_2H_3O_2)_2 + Cu(C_2H_3O_2)_2 + 6H_2O$. The crystals are stable at the summer temperature and do not lose water of crystallisation when exposed over calcium chloride for 48 hours; decomposition, however, sets in at 60°. The salt cannot be recrystallised from water, and is not formed when solutions containing equimolecular proportions of its constituents are mixed together, since in both cases the resulting solution on cooling or on spontaneous evaporation yields crystals either of copper acetate or a mixture of the double salt and copper acetate until the solution contains the constituent salts in the ratio of 1 mol. of copper acetate to 3 mols. of calcium acetate; when this point is reached, crystals of the pure double salt begin to separate. The double salt can readily be prepared by dissolving 25 grams (1 mol.) of copper acetate and 66 grams (3 mols.) of calcium acetate in 350 c.c. of warm water; on cooling, the pure salt separates in quadratic forms, and the mother-liquor on concentration continues to yield pure crystals until 10 mols. of calcium acetate are present. W. P. W

ββ-Methylethylpropionic Acid. By P. v. ROMBURGH (*Rec. Trav. Chim.*, **6**, 150—156).—Secondary butylmalonic acid was prepared by heating ethyl sodiomalonate with secondary butyl iodide for several hours. The ethyl secondary butylmalonate obtained on fractionation of the crude product, is a colourless liquid of a pleasant odour; it boils at 233—234° under a pressure of 774 mm.; sp. gr. at 75 = 0·988. When heated with alcoholic potash, acidified with hydrochloric acid, and extracted with ether, it yields *secondary butylmalonic acid*, $CHMeEt{\cdot}CH(COOH)_2$, which forms compact, transparent crystals melting at 76° and becoming opaque in the air. It dissolves readily in water, ether, alcohol, and boiling benzene. With ammonium chloride and calcium chloride, it gives a precipitate almost insoluble in boiling water. The silver salt is white.

When secondary butylmalonic acid is gradually heated to 200°, it gives off carbonic anhydride, and yields *ββ-methylethylpropionic acid*, $CHMeEt·CH_2·COOH$, which boils at 196—198° under a pressure of 762 mm., and is optically inactive; sp. gr. at 15° = 0·930; vapour-density 3·99. The silver salt crystallises from hot water in curved needles; the calcium salt forms transparent needles which contain 3 mols. H_2O, and become opaque when exposed to dry air. The *amide*, prepared by Hofmann's method, forms long, transparent needles which melt at 124°, and can be sublimed without altering the melting point. It dissolves in warm water, in alcohol, ether, and boiling benzene.

The author concludes that ββ-methylethylpropionic acid has the same constitution as the caproic acid from the dextrogyrate hexyl alcohol obtained from Roman essence of camomile, but differs from it in being optically inactive. This alcohol would therefore have the constitution $CHMeEt·CH_2·CH_2·OH$. C. H. B.

Borneo Tallow. By A. C. Geitel (*J. pr. Chem.* [2], **36**, 515—518).—The author has examined an authentic sample of Borneo tallow (the produce of *Shorea stenoptera* and other dipterocarpons), from Java. It had a bright-green colour, which by long exposure to the air became at first yellow, and eventually white. At ordinary temperatures, it had the consistence of cacao-butter, which it somewhat resembled in taste and smell. It softened between the fingers, commenced to melt at 35—36°, and became perfectly fluid at 42°. On cooling, the oil did not solidify until the temperature had fallen considerably below the melting point. A portion of the tallow was saponified with potash, and the resulting soap decomposed with dilute sulphuric acid; the mixture of fatty acids thus obtained crystallised well, and, after repeated washings with warm water and careful drying, solidified at 54°. It consisted almost entirely of stearic and oleic acids, present in the ratio of two to one. The tallow contained about 10 per cent. of free stearic acid, and yielded a like quantity of glycerol. The author points out that the composition of Borneo tallow, and the ease with which it can be saponified, render it particularly well adapted to the manufacture of soap and candles.

G. T. M.

Action of Nitric Acid on Amides and Alkylamides. By A. P. N. Franchimont (*Rec. Trav. Chim.*, **6**, 140—149).—When nitric acid acts on amides and methylamides, it would seem that the radicle of the organic acid is displaced by that of nitric acid, or in other words, by NO_2, but the amide of nitric acid is only stable when the two hydrogen atoms of the group NH_2 are displaced by a hydrocarbon radicle such as methyl. The three typical reactions may be represented by the equations: $AcNH_2 + HNO_3 = AcOH + N_2O + H_2O$; $AcNHMe + 2HNO_3 = AcOH + MeNO_3 + N_2O + H_2O$; and $AcNMe_2 + HNO_3 = AcOH + Me_2N·NO_2$.

Heptylamide, prepared by Hofmann's method and treated with the strongest nitric acid, yields a volume of nitrous oxide corresponding with 1 mol. of the amide; acetylglycocine behaves in a similar way. All compounds containing acetyl are not attacked, but in the majority of cases when any reaction takes place, the acetyl-group is removed in the form of acetic acid, as in the case of the amides. The same reaction seems to take place with propane-derivatives.

Strong sulphuric acid does not decompose the amides in the same way as nitric acid. In most cases the reaction in question does not occur between the free amides and nitric acid, but between the acid and nitrates of the amides which are first formed. It is possible that the nitric acid merely acts as a dehydrating agent, and this view would seem to be supported by the fact that sulphuric acid decomposes the nitrates of the amides in a precisely similar way. It is probable, however, that a sulphate is first formed, and the decomposition which ensues is due to the liberated nitric acid, and in fact if an amide is dissolved in sulphuric acid, there is no action beyond the formation of a sulphate, but on adding nitric acid decomposition at once begins. When the organic acid is not liberated, a stable nitro-derivative is formed, as in the case of dimethyloxamide. In other cases, a nitro-derivative may be formed in the first instance, but decomposes immediately. The action of acetic chloramide on silver nitrite yields acetic acid and nitrous oxide, a nitro-derivative possibly being formed as an unstable intermediate product.

Another possible supposition is that the action of nitric acid on nitrates of the amides is analogous to the formation of diazo-derivatives, and that unstable oxydiazo-compounds are formed; thus, for instance, $AcNH_3{\cdot}O{\cdot}NO_2$ gives $AcNH(O{\cdot}NO_2) : NO{\cdot}OH$; these oxydiazo-derivatives decomposing in accordance with the equations already given. This latter view is supported by the fact that a solution of dimethyloxamide in nitric acid evolves nitrous oxide after some time; that a solution of dinitrodimethyloxamide in nitric acid undergoes no change, and that if a solution of dimethyloxamide in nitric acid is poured into water immediately after its preparation, some little time elapses before the nitro-derivative separates.

No one supposition, however, is capable of explaining all cases. The main point is that the nature of the reaction is to a great extent determined by the nature of the acid radicle in the amide, and in some cases the nature of the alkyl radicles substituted in the NH_2-group exerts a distinct influence, ethyl and methyl-derivatives not behaving in exactly the same way.

C. H. B.

Isomerism of Fumaric and Maleïc Acids. By R. Anschütz (*Ber.*, **21**, 518—520).—Lossen (*Ber.*, **20**, 3310) suggests that the oxidation of fumaric and maleïc acids to tartaric and inactive tartaric acids may be explained with the help of the formulæ

$$COOH{\cdot}CH : CH{\cdot}COOH \text{ and } COOH{\cdot}C{\cdot}CH_2{\cdot}COOH,$$

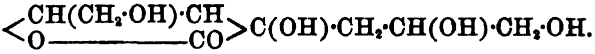
usually ascribed to fumaric and maleïc acids respectively. In the present paper, the improbability is shown of inactive tartaric acid having the constitution represented in the formula $COOH{\cdot}C(OH)_2{\cdot}CH_2{\cdot}COOH$ (which would follow from the formula adopted for maleïc acid), on the ground that it does not react with phenylhydrazine, and further that the ethyl salt of inactive tartaric is very different in its behaviour to Wislicenus's ethyl oxalacetate, $COOEt{\cdot}CO{\cdot}CH_2{\cdot}COOEt$. Ethyl oxalacetate boils at 120°, and the ethyl salt of inactive tartaric acid at 156° (both under 14 mm. pressure). The latter salt still contains two hydroxyl-groups, and when saponified with lime-water yields the characteristic calcium salt of inactive tartaric acid.

The only alternative formula for inactive tartaric acid is one in which two alcoholic hydroxyl-groups are represented as attached to two different carbon-atoms. The formation of an acid having this formula by the oxidation of maleïc acid, gives no support to the formula $COOH{\cdot}C{\cdot}CH_2{\cdot}COOH$ for the latter compound.

Having in view the observations of Brühl (Abstr., 1887, 1005) on the molecular refraction of aldehyde and paraldehyde, the author points out that differences in the molecular refraction of the ethyl salts of fumaric, maleïc, mesaconic and citraconic acids (Knops *Inaug. Diss.*, Bonn, 1887) harmonise with the formulæ for these compounds which he supports (compare also Abstr., 1887, 916). N. H. M.

Oxidation of Diallyloxalic Acid. By P. BULITSCH (*J. Russ. Chem. Soc.*, 1887, 73—97).—The action of oxidising agents on diallyloxalic acid was investigated by Saytzeff and Schatzky, but formic, carbonic, and oxalic acids were the only products obtained. From the analogy of this acid to dimethyloxalic, diethyloxalic, and diisopropyloxalic acids, it might be inferred that on oxidation a ketone would first be formed, which would subsequently split up into acids with a lower number of carbon-atoms than the original acid. It also seemed desirable to ascertain whether citric acid is formed in the reaction, as was supposed by Schatzky.

In order to study the products of the limited oxidation of diallyloxalic acid, it was treated with very dilute nitric acid. For this purpose diallyloxalic acid (10 grams) was acted on by a mixture of nitric acid (65 grams) of sp. gr. 1·155 with an equal quantity of water, at as low a temperature as possible. When the action was complete, the greater part of the nitric acid was expelled by careful evaporation, and after removing the oxalic acid by means of barium carbonate, the filtrate was boiled with a strong solution of baryta. On cooling, a yellow barium salt separated; this, after being washed, was dissolved in aqueous acetic acid, precipitated hot with lead acetate, and the precipitate decomposed with hydrogen sulphide. The filtrate was concentrated and a mixture of alcohol and ether added to remove inorganic impurities. On evaporating the clear solution, a brownish or yellow syrup was obtained, which did not solidify at −20°, and could not be distilled with aqueous vapour without decomposition. It is insoluble in ether, chloroform, and carbon bisulphide, but easily soluble in alcohol or water. It reduces Fehling's solution on warming, but this may be due to some admixture; silver salts, however, are not reduced. Its reaction is feebly acid. Repeated analyses point to the formula $C_8H_{14}O_6$, and its constitution, that of *tetrahydroxyoctolactone*, may be represented by the formula—



$$<\begin{matrix}CH(CH_2{\cdot}OH){\cdot}CH\\O\text{————————}CO\end{matrix}>C(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

Of the metallic derivatives, the potassium, sodium, ammonium, lead and silver salts, could not be obtained in a state fit for investigation. By the action of barium or calcium carbonate at the ordinary temperature, the corresponding derivatives were obtained in the form of amorphous, gummy masses, which are easily powdered when dry. After drying in the desiccator, the derivatives have the formula $(C_8H_{15}O_7)_2Ba$ and $(C_8H_{15}O_7)_2Ca$, whereas on drying at 100° they lose 2 mols. H_2O, becoming $(C_8H_{13}O_6)_2Ba$ and $(C_8H_{13}O_6)_2Ca$ respectively. The constitution of the salts, dried at the ordinary temperature, is represented (where $ba = \frac{1}{2}Ba$), by the formula

$$[OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2]_2{\cdot}C(OH){\cdot}COO\mathit{ba},$$

the salt of a pentahydroxy-acid. After drying at 100°, the salt is only soluble in water with great difficulty, and no longer takes up the elements of water. On boiling the tetrahydroxyoctolactone with calcium or barium carbonates, basic salts are obtained, which, when dried in the desiccator, have the formulæ $C_8H_{16}O_8Ba$ and $C_8H_{16}O_6Ca$, and after drying at 100° become $C_8H_{12}O_6Ba$ and $C_8H_{12}O_6Ca$. The loss of 2 mols. H_2O is analogous to that mentioned in the first instance. When the lactone is boiled with aqueous baryta, a still more basic salt is obtained, having the formula $C_8H_{15}O_8\mathit{ba}_3$ (dried in the desiccator) and $C_8H_{13}O_7\mathit{ba}_3$ (dried at 100°). The calcium salt prepared in an analogous manner is, however, identical with that obtained with calcium carbonate (see above). The original lactone could be easily regenerated from the basic barium salt by transforming it into the lead salt, and decomposing the latter with hydrogen sulphide. Cold water is without action on tetrahydroxyoctolactone, but warm water dissolves it and the corresponding pentahydroxydipropylacetic acid seems to be formed. The lactone does not unite with iodine or hydrochloric acid, this being in accordance with the saturated character of the compound. The most careful oxidation with a very weak solution of potassium permanganate in alkaline solution (1 per cent.) yielded carbonic and oxalic acids only. B. B.

Action of Sulphuric Acid on Diallyloxalic Acid. By P. BULITSCH (*J. Russ. Chem. Soc.*, 1887, 97—106).—In order to study the hydration of diallyloxalic acid, and to compare the product obtained with tetrahydroxyoctolactone, the former was treated with sulphuric acid. For this purpose, sulphuric acid of 66° B. is added drop by drop to diallyloxalic acid cooled with snow, when the mixture becomes brown, and some gas is evolved. The reaction is accelerated by warming the mixture gently from time to time, and cooling again immediately.

After addition of water, the liquid is boiled and saturated with barium hydroxide; the filtrate from the barium sulphate is then extracted with ether, which on evaporation leaves an oily liquid; this is a mixture of a saturated with an unsaturated lactone, the latter being more easily soluble in ether than the former. In order to separate the two, the product obtained as above is boiled with water, and the unsaturated lactone taken up from the solution by extracting it twice (not more) with ether. After removing sulphuric acid from the aqueous solution by means of baryta and the excess of the latter by carbonic anhydride, the filtrate is concentrated by evaporation, and decomposed with sulphuric acid. The filtrate from the barium sulphate is again extracted with ether. The remaining liquid, containing the saturated lactone, is neutralised with lead carbonate, filtered, and after separating the lead in solution by hydrogen sulphide and precipitating the mineral salts with alcohol and ether, the saturated lactone is obtained. Its composition is $C_8H_{14}O_4$. It is a syrupy liquid, soluble in alcohol and ether, and having a feebly acid reaction, a bitter taste, and an agreeable odour, especially on gently warming. It does not reduce Fehling's solution. It forms an amorphous barium-derivative, $(C_8H_{15}O_5)_2Ba$, which does not lose water at 120°, and is the salt of a trihydroxy-acid.

The formula of the unsaturated lactone (which is much more soluble in ether than the saturated compound) is $C_8H_{12}O_3$, and it forms a barium-derivative, $(C_8H_{13}O_4)_2Ba$, not losing water at 120°, and a corresponding calcium-derivative. The saturated lactone is a dihydroxylactone, the unsaturated a monohydroxylactone.

When the saturated lactone, $C_8H_{14}O_4$, the product of hydration of diallyloxalic acid, is subjected to a further treatment with sulphuric acid, a dehydration takes place, the unsaturated lactone, $C_8H_{12}O_3$, being formed. The supposed structure of the lactones in question was confirmed by Hübel's test. B. B.

Mucohydroxybromic and Mucohydroxychloric Acids. By H. B. Hill and A. W. Palmer (*Amer. Chem. J.*, 9, 147—174).—Reference is made to former work (Abstr., 1879, 224; 1884, 731; 1885, 531) on the decomposition of mucobromic acid by baryta and by potassium phenoxide. The constitution of the mucohydroxybromic and mucohydroxychloric acids is represented by the formula

$$COOH\cdot C(OH)\colon CX\cdot COH,$$

their bibasic characters being due to the environment of the hydroxyl-group; the aniline-derivatives are represented by the formula $COOH\cdot C(OH)\colon CX\cdot CH\colon NPh$, that is, as analogous to Böttinger's anilglyoxylic acid (Abstr., 1879, 51).

Mucohydroxybromic acid, $C_4H_3BrO_4$, is best obtained from mucobromic acid by very cautious treatment with baryta at a low temperature (yield 60 per cent.). The free acid is obtained by mixing the equivalent of sulphuric acid with the powdered barium salt, and evaporating in a vacuum. It is crystalline, melts at 111—112°, and its solution decomposes readily. The barium salt, $BaC_4HBrO_4 + 2H_2O$, is sparingly soluble in water, and decomposes readily when heated; an acid salt could not be obtained. The potassium salt, $K_2C_4HBrO_4 + H_2O$, and the silver salt, $Ag_2C_4HBrO_4$, are described, as well as the dimethyl, diethyl, and monethyl salts, $C_4H_2BrO_4·Et$, only the last was obtained in crystals; it melts at 88—89°.

When the barium salt is boiled with baryta-water, carbonic, oxalic, formic, and hydrobromic acids are formed, together with an acid yielding a gummy barium salt.

The oxidation of mucohydroxybromic acid is best effected by bromine-water; oxalic acid, bromal hydrate, and hydrobromic acid are formed.

With phenylhydrazine or hydroxylamine, no definite compound with mucohydroxybromic acid could be obtained, but with the primary aromatic amines and carbamide crystalline condensation-products are readily formed.

Anilmucohydroxybromic acid, $C_4H_3BrO_3·NPh$, is most readily obtained by dissolving barium mucohydroxybromate in hydrochloric acid and adding aniline hydrochloride; it crystallises in pale-yellow needles, sparingly soluble in cold water, and melts at 131—132°. The salts $Ba(C_{10}H_7BrNO_3)_2 + \frac{1}{2}H_2O$, $K_2C_{10}H_6BrNO_3$, $Ag_2C_{10}H_6BrNO_3$, and a monobasic silver salt, are described; they are yellow and crystalline. With phenylhydrazine a crystalline compound,

$$C_{10}H_8BrNO_3,C_6H_8N_2,$$

is formed without elimination of water; it is very readily decomposed.

Mucohydroxychloric acid, $C_4H_3ClO_4$.—It has been previously shown that when treated with baryta, mucochloric acid yields α-β-dichloracrylic and formic acids, but it is now shown that by adding the baryta only as fast as it is acted on, and at a low temperature, 73 per cent. of the theoretical yield of barium mucohydroxychloric acid is obtained, along with some α-β-dichloracrylic acid. The free acid is obtained like the corresponding bromine compound; it is, however, more stable, and melts at 114—115°. The barium salt, $BaC_4HClO_4 + 2H_2O$, on keeping, changes to a more stable form, containing only 1 mol. H_2O; the potassium and silver salts are anhydrous; the monethyl salt is crystalline, melting at 94—95°; but the diethyl salt is a viscous liquid. The barium salt, when heated with excess of baryta-water, is decomposed in just the same way as the mucohydroxybromic acid; there is no simple relation between the quantities of oxalic and carbonic acids formed. Bromine-water also decomposes the acid, just as it does the bromo-acid.

Anilmucohydroxychloric acid, $C_4H_3ClO_3·NPh$, is obtained in like manner to the corresponding bromine-compound; it contains 1 mol. H_2O, which is readily given off over sulphuric acid, or at 100°; it is brilliant yellow, and melts with decomposition at 145—147°. The three salts, $Ba(C_{10}H_7ClNO_3)_2 + \frac{1}{2}H_2O$, $Ag_2C_{10}H_6ClNO_3$, and $K_2C_{10}H_6ClNO_3$, are described. With phenylhydrazine it forms a compound,

$$C_{10}H_8ClNO_3·C_6H_8N_2,$$

readily decomposed by acids or alkalis. H. B.

Murexoïn. By O. Brunn (*Ber.*, **20**, 513—518).—Murexoïn (Rochleder, *J. pr. Chem.*, **51**, 405) is prepared as follows:—Caffeïne is converted by Fischer's method (Abstr., 1882, 217) into dimethylalloxan, which is reduced by hydrogen sulphide to tetramethylalloxantin. This is finely powdered, and in portions of 5 grams moistened and spread on a plate, and exposed to the action of air and ammonia until the whole acquires a dark-brown colour. The murexoïn is afterwards crystallised from hot water; the yield is almost quantitative. It is rather sparingly soluble in water with an intense colour resembling that of potassium permanganate, crystallises in slender prisms, and sublimes at about 230° without decomposition. When evaporated down with dilute hydrochloric acid, it decomposes into dimethylparabanic acid and another compound which could not be purified. N. H. M.

Vapour-density of Aluminium Ethide. By L. Roux and E. Louise (*Compt. rend.*, **106**, 73—75).—The aluminium ethide was obtained by the action of mercuric ethide on aluminium in sealed tubes; it boiled at 195—200°. The vapour-density was determined by Meyer's method in an atmosphere of pure and dry nitrogen, the apparatus being heated by different liquids of known boiling points. The following results were obtained:—

Temperature........	235°	258°	310°	350°
Vapour-density......	8·1	6·2	2·5	2·5

It is evident that near its boiling point the vapour-density is normal, but at a higher temperature the compound dissociates, and the density is reduced to one-third. Most probably the compound splits up in accordance with the equation $Al_2Et_6 = 2AlEt_2 + C_4H_{10}$.

C. H. B.

Condensation of Furfuraldehyde with Chloraldehyde. By P. Mehne (*Ber.*, **21**, 423—428).—*Chlorofurfuracraldehyde*,

$$C_4H_3O{\cdot}CH{:}CCl{\cdot}CHO,$$

is prepared by slowly adding 10 per cent. aqueous soda to mixed aqueous solutions of furfuraldehyde and chloracetaldehyde. It crystallises in broad, yellow, lustrous needles, melts at 79°, is soluble in hot water, ether, alcohol, benzene, light petroleum, and chloroform, and can be distilled with steam. The phenylhydrazine-derivative forms golden-yellow plates, begins to decompose at 142°, and melts at 157°. The *oxime* crystallises in small, white, interlaced needles, begins to sublime with decomposition at about 110°, and melts at 164—165°.

γ-*Chlorofurfuracrylic acid*, $C_4H_3O{\cdot}CH{:}CCl{\cdot}COOH$, is prepared by heating the aldehyde with moist silver oxide for some days in a reflux apparatus; it crystallises in tufts of white needles, melts at about 142°, but sinters at a lower temperature. It is soluble in water, alcohol, ether, benzene, and chloroform, insoluble in light petroleum.

γ-*Chlorofurfurpentic acid*, $C_4H_3O{\cdot}CH{:}CCl{\cdot}CH{:}CH{\cdot}COOH$, is prepared by heating to boiling 4 parts of γ-chlorofurfuracraldehyde, 3 parts of anhydrous sodium acetate, and 5 parts of acetic anhydride, for three hours in a reflux apparatus. It forms clear yellow, interlaced needles, melts at 168°, and is soluble in alcohol, ether, benzene, and chloroform, insoluble in light petroleum. With concentrated sulphuric acid, it gives a reddish-brown coloration, changing to reddish-violet. A. J. G.

Polymerisation-products of the Tolyl Cyanates. By W. FRENTZEL (*Ber.*, **21**, 411—414).—*Diparatolyl dicyanate*, $C_2N_2O_2(C_7H_7)_2$, is obtained by the action of a few drops of triethylphosphine on tolyl cyanate; it melts at 185° with dissociation into the cyanate. Proof of the substance being the dicyanate is given by its reaction with absolute alcohol, which converts it into an allophanate; this crystallises in needles, and melts at 111°.

Paratolyl cyanurate, $C_3N_3O_3(C_7H_7)_3$, is prepared by heating the cyanate with potassium acetate at 100° for five hours; it forms white needles, and melts at 265° without decomposition.

Orthotolyl cyanurate is readily obtained by the action of potassium acetate on orthotolyl cyanate; it is white, crystalline, and suffers but slight decomposition on fusion. The corresponding dicyanate could not be obtained, the action of triethylphosphine on the cyanate only leading to a very partial polymerisation into the cyanurate.

A. J. G.

β-Nitrocymene. By A. F. HOLLEMAN (*Rec. Trav. Chim.*, **6**, 60—86).—20 grams of cymene is mixed with 200 grams of fuming nitric acid of sp. gr. 1·4, and the two layers of liquid are gradually mixed by passing a current of air into them, the temperature not rising above 50°. On pouring into water, a viscous, semi-solid mass is precipitated, which is separated by filtration through glass-wool by means of a pump. The crystals thus obtained are recrystallised from carbon bisulphide. They have the composition $C_9H_8NO_2$ (comp. Abstr., 1886, 1017), melt at 125°, and explode at about 160° in a vacuum. They dissolve readily in acetic acid and warm alcohol, in acetone, benzene, chloroform, carbon bisulphide, and ether, and are slightly soluble in cold alcohol and in boiling light petroleum. The compound separates from all the ordinary solvents in small, radiating needles. Its molecular weight as determined in acetic acid solution by Raoult's method is about 324, which agrees with the formula $C_{18}H_{16}N_2O_4$. With aqueous potash, it yields potassium paratoluate; with alcoholic potash, the products are ammonia, ethyl paratoluate boiling at 230—233°, and potassium paratoluate, but no hydrocyanic acid, cyanuric acid, nitrous or nitric acids. It follows that the nitrogen does not exist in the benzene-ring, and the methyl-group remains intact, and it would seem that the nitrogen has been substituted in the propyl side-chain of the cymene.

Sulphuric acid dissolves the so-called nitrocymene at 50°, and converts it into paratoluic acid. Sodium amalgam in warm alcoholic solution converts it into sodium paratoluate. Stannous chloride in presence of dilute alcohol produces hydrocyanic acid, ethyl paratoluate, and paratoluic acid.

If the nitrocymene is mixed with zinc-powder, added gradually to acetic acid, and the solution afterwards poured into water, a white or grey, flocculent precipitate is obtained, and if this is recrystallised from alcohol it yields small, pink needles of the composition $C_{18}H_{18}O_3$, which melt at 159°, but cannot be sublimed. This compound is very slightly soluble in cold ethyl alcohol or light petroleum, somewhat soluble in boiling alcohol or benzene, insoluble in concentrated hydrochloric acid or in alkalis. This product of reduction differs from nitrocymene in containing H_2 in place of N_2O_2, and it follows that the nitrogen does not exist in nitrocymene in the form of a nitroxyl-group. With acetic chloride, the product of reduction yields a substance of the composition $C_{18}H_{16}O$, which crystallises from alcohol in small, highly lustrous, white needles, melting at 164°. The acetic chloride acts as a dehydrating agent.

If the compound $C_{18}H_{18}O_2$ is dissolved in concentrated acetic acid and boiled with ammonium acetate, it yields bluish crystals of the composition $C_{18}H_{17}N$, melting at 197°. The action of ammonia is similar to that which it exerts on paradiketones, and the product may be regarded as *diparatolylpyrroline.* With hydrochloric acid, it yields a cherry-red resin soluble in alcohol, and with isatin it gives an intense red coloration after some days.

When heated at 170—180° in sealed tubes for half an hour with an equal weight of phosphorus pentasulphide, the compound $C_{18}H_{18}O$ yields hydrogen sulphide and *diparatolylthiophen*, $C_{18}H_{16}S$, which crystallises in small, white plates melting at 171°. With isatin, it gives an intense dark-green coloration. The properties of the product of reduction, $C_{18}H_{18}O_2$, agree with those of diketones, and it probably has the constitution $C_6H_4Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4Me$.

If 100 grams of toluene and 30 grams of succinic chloride are added to 100 grams of aluminium chloride just covered with carbon bisulphide, and the product crystallised from acetic acid and from alcohol, small, reddish needles are obtained, identical with the product of reduction of β-nitrocymene. This result agrees with the constitution ascribed to the compound. Neither nitric nor nitrous acid converts it into β-nitrocymene.

β-Nitrocymene was treated with strong alcoholic ammonia, and the product evaporated to dryness on the water-bath and treated with ether. A white substance (A) remains undissolved, and some of the same substance is soluble in ether. The ethereal solution contains a second substance (B), which is insoluble in boiling benzene, whilst (A) is soluble; they can thus be separated. After purification by crystallisation from water or alcohol, the substance (A) forms colourless, rectangular crystals of paratoluamide, which melt at 158—159°, and are converted into paratoluic acid and ammonia by hydrochloric acid. This product is identical with paratoluamide prepared by heating ammonium paratoluate in sealed tubes at 230°. The product (B) seems to have the composition $C_{10}H_9N_3O_2$, melts at 162°, and is insoluble in acids and alkalis.

Hydrochloric acid in sealed tubes at 140° converts β-nitrocymene into ammonium chloride, paratoluic acid, carbonic anhydride, and carbonic oxide. The prolonged action of boiling hydrochloric acid produces paratoluic acid and hydroxylamine, with a small quantity of oxalic acid.

Paratolyl methyl ketone, prepared by Claus and Wollner's method, when carefully mixed with 10 times its weight of nitric acid of sp. gr. 1·4, poured into water and the product crystallised from alcohol, yields small needles identical with β-nitrocymene. From this result it follows that β-nitrocymene contains two tolyl-groups. The presence of the group C(NOH)·C(NOH) is rendered probable by the formation of oxalic acid on treatment with hydrochloric acid, and the formation of carbonic anhydride and carbonic oxide when it is treated with the same acid in sealed tubes. The production of hydrocyanic acid on treatment with stannous chloride indicates that carbon is in direct union with the nitrogen, and the formation of ammonia and hydroxylamine points to the presence of the oximido-group. So-called β-nitrocymene therefore seems to be symmetrical *diparatolyldiisonitrosoethane*, $C_6H_4Me{\cdot}CO{\cdot}C(NOH){\cdot}C(NOH){\cdot}CO{\cdot}C_6H_4Me$.

With acetic anhydride, it yields rhombic crystals of the composition $C_{18}H_{14}N_2O_4Ac_2$ or $C_{18}H_{14}N_2O_4,Ac_2O$, which melt at 167°, and if introduced into concentrated sulphuric acid give a red coloration which disappears on adding water, and does not reappear on neutralisation. Water converts it into paratoluic acid, and hence it would seem that the acetyl-group has not really entered into combination.

C. H. B.

Chlorophenols. By A. Mosso (*Chem. Centr.*, 1887, 1396; from *Ann. Chim. Farm.*, **87**, 184—191).—From equal molecular weights of metadichlorophenol and phthalic chloride, metadichlorophenyl phthalate, $C_6H_4(COO{\cdot}C_6H_3Cl_2)_2$, was obtained. It forms white needles melting at 108°. The *benzoate* forms white plates melting at 97°.

Orthochlorophenyl benzoate is a liquid which boils at 312—315°, and does not solidify below 0°; the *phthalate* after crystallisation from alcohol melts at 98°. *Chlorophenyl benzoate* melts at 93°; the *phthalate* melts at 11°. *Metachlorophenyl benzoate*? melts at 86°, and the *phthalate* at 108°.

J. P. L.

Dibromonitrosophenol. By O. Fischer and E. Hepp (*Ber.*, **21**, 674—675).—*Diorthobromonitrosophenol*,

$$C_6H_2Br_2O{:}NOH\ [O : Br_2 : NOH = 1 : 2 : 6 : 4],$$

is prepared by the action of bromine on an alcoholic solution of nitrosophenol; it crystallises in small, lustrous plates, is readily soluble in alcohol and ether, more sparingly in chloroform and acetic acid, yields an amorphous potassium-derivative, and when reduced is converted into Hölz's diorthobromoparamidophenol. The statement previously made (Abstr., 1887, 1105), that aniline converts the dibromo-derivative into a brominated azophenine, is incorrect; on further purification, all the bromine is removed and the product melts at 197—198°, and judging from its properties it is an oxyazophenine. The bromine in dibromonitrosophenol is very loosely combined.

A. J. G.

Benzyl Chloracetates. By K. Seubert (*Ber.*, **21**, 281—285).—To obtain these salts, a mixture of the calculated quantities of benzyl alcohol and the chloracetic acid, to which an excess of one of the constituents had been added, was allowed to remain for several days, then saturated with hydrogen chloride, and finally heated on a water-bath. The product, after washing with water and drying over calcium chloride, was fractionated under reduced pressure in a Meyer's apparatus (Abstr., 1887, 884), and the distillate, after treatment with precipitated calcium carbonate to remove any acid present, was refractionated in a vacuum. Even under these conditions, a slight decomposition occurred. The products are colourless, strongly refractive liquids, insoluble in water, and readily soluble in alcohol and ether. The odour is strongly aromatic and persistent.

Benzyl chloracetate, $CH_2Cl{\cdot}COOC_7H_7$, boils at 147·5° at 9 mm., and has a sp. gr. = 1·2223 at 4°/4°. Its refractive index $n_D = 1{\cdot}5246$ at 18° (that of water being = 1·333), and its dispersion coefficient $\delta_n = 0{\cdot}010272$. *Benzyl dichloracetate*, $CHCl_2{\cdot}COOC_7H_7$, boils at 179° at 60 mm., and has a sp. gr. = 1·313 at 4°/4°. Its refractive index $n_D = 1{\cdot}5268$ at 17·7°, and its dispersive coefficient $\delta_n = 0{\cdot}010275$. *Benzyl trichloracetate*, $CCl_3{\cdot}COOC_7H_7$, boils at 178·5° at 50 mm. pressure, and has a sp. gr. = 1·3887 at 4°/4°. Its refractive index $n_D = 1{\cdot}5288$ at 18·8°, and its dispersion coefficient $\delta_n = 0{\cdot}010191$. According to Persoz' rule, the calculated boiling points of the three compounds at the ordinary pressure are 269·5°, 275·5°, and 279·5° respectively. In the following table the calculated values of the specific and molecular refraction for each compound are obtained by regarding the three "double bonds" of the benzene nucleus as equivalent to six "single bonds."

Salt.	$M\left(\frac{n-1}{d}\right)$.		$\frac{M}{d}\left(\frac{n^2-1}{n^2+2}\right)$.	
	Found.	Calculated.	Found.	Calculated.
Benzyl chloracetate..........	78·98	78·6	45·85	46·96
Difference	8·64	8·6	5·27	4·98
Benzyl dichloracetate........	87·62	87·2	51·12	51·94
Difference	8·63	8·6	5·00	4·98
Benzyl trichloracetate........	96·25	95·8	56·12	56·92

W. P. W.

Trimethoxybenzenes and the Constitution of Asarone. By W. Will (*Ber.*, **21**, 602—616).—1.3.5 *Trimethoxybenzene* (*phloroglucinol trimethyl ether*) is prepared by first passing hydrogen chloride into a solution of phloroglucinol in methyl alcohol, and then completely methylating the dimethyl ether so obtained with methyl iodide and potash. It forms colourless crystals, melts at 52·5°, boils at 255·5° (corr.) without decomposition, is insoluble in water and alkalis, readily soluble in alcohol, ether, and benzene. The *tribromo*-derivative, $C_6Br_3(OMe)_3$, forms long, colourless needles, melts at 145°, and when treated with concentrated nitric acid, yields golden plates of the nitrate of a colourless base, which will be described later.

1 : 2 : 4 *Trimethoxybenzene* (*hydroxyquinol trimethyl ether*).—The method by which the ethyl compound was prepared by Will and Pukall (Abstr., 1817, 660) did not prove successful with the methyl compound. The monomethyl ether of benzeneazoresorcinol was readily

obtained in dark-red needles melting at 114°, but such difficulty was experienced in converting this into the dimethyl ether (yellowish-red needles melting at 75°) that another method had to be adopted. Its preparation was at last effected by the methylation of methoxyquinol. 1 : 2 : 4 Trimethoxybenzene is a colourless oil which cannot be solidified in a freezing mixture, and boils at 247° (corr.). When treated with concentrated nitric acid, it yields a *dinitro*-derivative, forming brownish needles insoluble in cold water and dilute acids.

Methoxyquinone, $C_6H_3O_2{\cdot}OMe$ [$OMe : O_2 = 1 : 3 : 6$], is obtained by oxidising orthanisidine with chromic mixture. It crystallises in slender, yellow needles, melts at 140°, sublimes readily, is sparingly soluble in water, readily in alcohol, very readily in alkalis, and yields an *anilide* when gently heated with aniline in acetic acid solution.

Methoxyquinol, $C_6H_3(OH)_2{\cdot}OMe$, is prepared by reducing the quinone with sulphurous acid. It forms colourless plates, melts at 84°, sublimes readily, and shows the properties characteristic of a quinol.

1 : 2 : 3 *Trimethoxybenzene* (*pyrogallol trimethyl ether*) is prepared by heating pyrogallol with excess of methyl iodide and potash dissolved in methyl alcohol, in a reflux apparatus. It crystallises in long, colourless needles, melts at 47°, and boils at 235° (corr.), is readily soluble in alcohol, ether, and benzene, insoluble in water and alkalis; the *tribromo*-derivative, $C_6Br_3(OMe)_3$, melts at 81·5°. When treated with concentrated nitric acid, it is converted into dimethoxyquinone and a nitro-derivative which forms thick prisms melting at 100°. A dinitro- and an amido-derivative were also prepared, melting at 126° and 114° respectively.

Dimethoxyquinone, $C_6H_2O_2(OMe)_2$, is separated from the accompanying nitro-ether by its sparing solubility in hot alcohol. It crystallises in thick prisms of golden lustre, melts at 249°, sublimes readily, and is sparingly soluble in hot water and ether, readily soluble in hot acetic acid. The *dibromo*-derivative forms yellowish-red, nacreous plates melting at 175°, and when reduced yields the corresponding dibromoquinol melting at 137°.

Dihydroxydimethoxybenzene is obtained by the action of sulphurous acid on the quinone. It forms lustrous, spear-shaped crystals, melts at 158°, dissolves in alkalis with green colour, and is reconverted into the quinone on oxidation.

Tetramethoxybenzene is obtained by the action of methyl iodide and potash on the preceding compound; it forms lustrous plates, melts at 47°, boils at 271°, and is readily soluble in alcohol, ether, benzene, and acetic acid, insoluble in water; the *dibromo*-derivative melts at 76°. When oxidised, it yields the dimethoxyquinone melting at 249°, together with another compound not yet investigated.

The trimethoxybenzene obtained from asarone is identical with the 1 : 2 : 4 trimethoxybenzene described above; it follows, therefore, that asarone has the constitution $C_3H_5{\cdot}C_6H_2(OMe)_3$ [$C_3H_5 : (OMe)_3 = 1 : 3 : 4 : 6$]. (Compare next Abstract.) A. J. G.

Asarone. By B. Rizza and A. Boutlerow (*J. Russ. Chem. Soc.*, 1887, 1—12).—In 1884 asarone was investigated by the authors (Abstr., 1884, 1042; 1885, 669), and found to be an unsaturated compound, containing three methoxyl-groups. The molecular formula, $C_{12}H_{16}O_3$, was ascribed to it. On oxidation, it yielded a neutral, crystalline substance; this was subsequently investigated by Staats, and although his work confirms the authors' results in general, the sample which he analysed does not seem to have been pure.

In the present paper, the chemical nature of asarone is determined by the study of its products of oxidation, which are a neutral substance, an acid, and a compound derived from the latter by the elimination of a CO_2 group. Two methods are employed. In the first, the asarone (12 grams) is dissolved in strong acetic acid (40 grams) and potassium dichromate (6 grams) added; the mixture is then carefully heated until it turns green. On cooling and adding water, needle-shaped crystals separate together with a reddish-brown, resinous substance. The crystals are neutral, of a silky lustre, soluble in hot water, ether, light petroleum, and benzene. They melt at 114°, but sublime even at 100°. The analysis agrees with the formula $C_{10}H_{12}O_4$. Better results are obtained by the use of potassium permanganate solution (40 grams in 750 grams water), which is added drop by drop to a warm solution of asarone (10 grams in 450 grams water). The compound $C_{10}H_{12}O_4$ is extracted from the filtrate by means of ether; the alkaline solution is then evaporated to dryness, and the residue either extracted with hot alcohol or decomposed with hydrochloric acid, and then extracted with alcohol. In the first case the potassium salt of a new acid separates out from the hot spirit, in the second the new acid itself. Carbonic, formic, oxalic, and acetic acids are formed at the same time. When the operation is conducted as described, the quantity of acid formed is much larger than that of the neutral substance, but the reverse is the case when a mixture of asarone (5 grams) and finely-powdered permanganate (7·5 grams) is added in small portions at a time to boiling water. The acid, $C_{10}H_{12}O_5$, crystallises in needles, which are soluble in benzene, light petroleum, alcohol, and boiling water. It melts at 144°, and boils about 300°; it has distinctly acid properties, decomposing carbonates. Its silver salt, prepared from the potassium salt, is tolerably stable under the influence of air and light.

The neutral substance, $C_{10}H_{12}O_4$, was found to be the aldehyde of the acid $C_{10}N_{12}O_5$, as was proved by the oxidising it with permanganate, when it was converted into the acid. Neither of these substances, however, has the properties of an unsaturated compound, so characteristically exhibited by asarone. That the neutral substance is an aldehyde is also proved by treating it with phenylhydrazine hydrochloride in the presence of sodium acetate, when yellow crystals are obtained, melting at 120—121°, and having the formula $C_{16}H_{18}O_3N_2$. By the action of sodium amalgam on the aldehyde, two new compounds are formed, one of which melts at 62°, the other at 102°. One of them seems to be the alcohol corresponding with the aldehyde, but they were not further investigated.

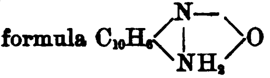
Three methoxyl-groups exist in asarone, and these are also present in the aldehyde and in the acid, as is shown by heating them with hydrochloric or hydrobromic acid, when methyl chloride or bromide is formed. It is best, however, to first heat the acid or aldehyde with four times its weight of slaked lime, whereby it is converted into an oily substance of the formula $C_9H_{12}O_3$, boiling at 245—247° ; this when heated with hydriodic acid in a sealed tube yields methyl iodide, corresponding in amount with three methoxyl-groups, from which it would appear that the constitution of this oil is $C_6H_3(OCH_3)_3$, that is, the trimethyl ether of a triatomic phenol. The presence of the benzene nucleus in asarone was proved by heating it with zinc-dust, and passing the products of distillation into strong nitric acid, when nitrobenzene was obtained.

The authors conclude from the study of the reactions of asarone and the allied compounds that their constitution may be expressed by the following formulæ: Asarone, $C_6H_2(OMe)_3{\cdot}CH{:}CH{\cdot}CH_3$; asarone dibromide, $C_6H_2(OMe)_3{\cdot}CHBr{\cdot}CHBr{\cdot}CH_3$; the aldehyde, $C_6H_2(OMe)_3{\cdot}CHO$; the acid, $C_6H_2(OMe)_3{\cdot}COOH$, and the oily substance by $C_6H_3(OMe)_3$. Without regard to the position of the single group in the benzene nucleus, a striking analogy exists between asarone, the aldehyde, and the acid from asarone, and anethoïl, $OMe{\cdot}C_6H_4{\cdot}C_3H_5$, anisic aldehyde, $OMe{\cdot}C_6H_4{\cdot}CHO$, and anisic acid, $OMe{\cdot}C_6H_4{\cdot}COOH$, on one side, and eugenyl methyl ether, $(OMe)_2{\cdot}C_6H_3{\cdot}C_3H_5$, vanilyl methyl ether, $(OMe)_2C_6H_3{\cdot}CHO$, and veratric or dimethylresorcinic acid, $(OMe)_2C_6H_3{\cdot}COOH$, on the other. The authors consider it a complicated task to determine the relative positions of the substituting groups. The acid and the trimethyl ether were treated with phosphorus pentachloride, hydriodic acid, and, lastly, with hydrochloric acid, but only in the last case was a satisfactory result obtained. The product crystallised from hot water in glistening needles, melting about 250°, decomposition and sublimation taking place at a much lower temperature. It dissolves in sulphuric acid, forming a blue, and in nitric acid a green solution. With ferric chloride, the aqueous solution gives a black coloration, which in dilute solution becomes violet on adding a little sodium hydrogen carbonate. Its composition corresponds with the formula $C_{12}H_8O_4 = 2C_6H_3(OH)_3 - 2H_2O$, and it is to a certain degree analogous to phloroglucol. B. B.

Paranitrosoaniline. By O. FISCHER and E. HEPP (*Ber.*, **21**, 684—686).—The preparation and some of the properties of this substance have been already described (Abstr., 1887, 1114). The sodium salt, $C_6H_6N_2O,NaOH + H_2O$, prepared by mixing alcoholic solutions of the nitroso-compound and soda, is a yellow, crystalline mass. Paraphenylenediamine is formed when nitrosoaniline is reduced with tin and hydrochloric acid. With hydroxylamine hydrochloride in alcoholic solution, it yields Nietzki and Kehrmann's quinonedioxime (Abstr., 1887, 575); this reaction seems common to all paranitroso-bases.

When nitrosoaniline is treated with phenylhydrazine hydrochloride, a compound, $C_{12}H_{14}N_4O$, is obtained, which crystallises in yellow needles, and when carefully heated melts at 125° with decomposition ; when more quickly heated it explodes. Similar compounds with phenylhydrazine seem to be given by all nitroso-bases.

Nitrosoaniline when heated with aniline hydrochloride (1 part) and aniline (5 parts) yields the azophenine which Kimich obtained from nitrosophenol and nitrosodimethylaniline.

α-Nitroso-β-ethylnaphthylamine (Abstr., 1887, 1114) is also formed by the action of excess of a dilute aqueous solution of ethylamine on α-nitroso-β-naphthol. That this substance is really a secondary base is shown by its conversion into the corresponding nitrosamine, $C_{12}H_{11}N_3O_2$, when treated with nitrous acid; this crystallises in yellowish-white, woolly needles, gives Liebermann's reaction, and decomposes at 105°; Ilinski's compound must be the primary base of the formula  $C_{10}H_6\left\langle\begin{matrix}N-\\ |\\ NH_2\end{matrix}\right\rangle O$ $[N : NH_2 = 1 : 2]$.

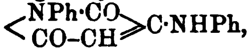
A. J. G.

Relation between the Constitution of Polybasic Unsaturated Organic Acids and the Formation of their Anilides. By A. MICHAEL and G. M. PALMER (*Amer. Chem. J.*, 9, 180—204).—The present means of distinguishing between acids of the maleïc and fumaric series, depending on the formation of the anhydrides, is very unsatisfactory, as it necessitates the use of a high temperature, whereby intermolecular changes may occur, is extravagant with the material, and, moreover, is not applicable to a large number of unsaturated acids. Gottlieb has observed that an aqueous solution of aniline citraconate when boiled is converted into citraconanil, whilst a solution of aniline mesaconate suffers no change on evaporation; it is now found that this distinction is general between the acids of the fumaric and maleïc series, as is shown by the following observations.

Maleïc dianilide, $C_2H_2(CO\cdot NHPh)_2$, is formed when maleïc anhydride, aniline, and water are heated together; it crystallises in long, white needles, melts at 211—212°, and is but sparingly soluble in cold water.

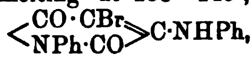
Maleïc monanilide, $COOH\cdot CH\colon CH\cdot CO\cdot NHPh$, is formed by allowing a solution of the acid aniline salt to remain at ordinary temperature; it melts at 207°.

Aqueous fumaric acid and aniline may be heated together in any proportion without anything else than the aniline salt being formed.

Bromomaleïc monanilide, $COOH\cdot CH\colon CBr\cdot CO\cdot NHPh$. Aqueous bromomaleïc acid when treated in the cold with aniline yields first the acid aniline salt, $COOH\cdot CH\colon CBr\cdot COONH_3Ph$, melting at 128°; the aqueous solution of this salt, if allowed to remain several days, deposits the anilide. If the treatment of the acid with aniline is effected with the aid of heat, entirely different products are formed; namely, a bright yellow substance, the *anil* of *phenylamidomaleïc acid*,  $\left\langle\begin{matrix}NPh\cdot CO\\ CO{-}CH\end{matrix}\right\rangle C\cdot NHPh$, melting at 229—230°, separates, and the mother-liquors deposit afterwards a lighter yellow substance, *phenylamidomaleïc monanilide*, $COOH\cdot C(NHPh)\colon CH\cdot CONHPh$, which is soluble in very dilute potash, the anil being insoluble.

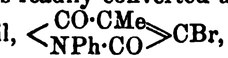
When cold aqueous bromofumaric acid is treated with aniline, the very insoluble acid aniline salt, $COOH\cdot CH\colon CBr\cdot COONH_3Ph$, melting at 153—154°, is formed. In contact with water or in solution, it does not change on keeping, but when boiled it deposits the yellow anil (m. p. 229—230°) just described.

Aqueous chlorofumaric acid and aniline easily yield the acid ammonium salt, $\mathrm{COOH\cdot CH\colon CCl\cdot COONH_3Ph}$, soluble in alcohol, sparingly in water, and melting at 178°. Its aqueous solution, or the solid in contact in water, may be left any length of time without decomposition; but when the solution is boiled for some time it is converted into the yellow anil of phenylamidomaleïc acid above described.

The acid aniline salt of dibromomaleïc acid is easily prepared; being very sparingly soluble; when allowed to remain under water, an anilide is gradually formed, but not in a state of purity. The normal aniline salt also is insoluble, and is gradually converted into an anilide, $\mathrm{NHPh\cdot CO\cdot CBr\colon CBr\cdot CO\cdot NHPh}$, melting at 138—140°, and when heated is converted into a yellow anil,  $<\begin{matrix}\mathrm{CO\cdot CBr}\\\mathrm{NPh\cdot CO}\end{matrix}>\mathrm{C\cdot NHPh}$, melting with decomposition at 182—183°.

The acid aniline salt of bromocitraconic acid,

$$\mathrm{COOH\cdot CMe\colon CBr\cdot COONH_3Ph},$$

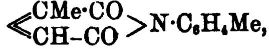
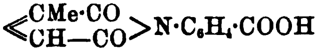
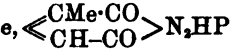
melting at 120—121°, is readily converted under water or by heating with water into the anil,  $<\begin{matrix}\mathrm{CO\cdot CMe}\\\mathrm{NPh\cdot CO}\end{matrix}>\mathrm{CBr}$, melting at 144·5—145·5°.

Dianiline aconitate when boiled in aqueous solution yields an anilide, $\mathrm{C_{18}H_{14}N_2O_3}$, forming yellow needles melting at 250—252°, and a quantity of an amorphous substance; better results are obtained by allowing the solution to remain at ordinary temperatures, when an anilide, $\mathrm{C_{18}H_{16}N_2O_4}$, melting at 188—189°, is formed; hence it is clear that aconitic acid belongs to the maleïc and not to the fumaric group.

Citraconic acid yields dimethylaniline and diethylaniline salts, which decompose readily on heating, but the formation of anilides has not been noticed. Itaconic acid behaves like citraconic acid with secondary and tertiary amines, but with aniline an anilide is formed. This difference may be made use of to separate primary from admixed secondary and tertiary amines.

Citraconic monanilide, $\mathrm{COOH\cdot CH\colon CMe\cdot CO\cdot NHPh}$, is easily obtained by allowing a solution of monaniline citraconate to stand in the cold; it melts at 175°, and is soluble in alkalis, but is reprecipitated by hydrochloric acid. Dianiline citraconate does not change in aqueous solution until boiled, when the anil separates; this melts at 98°.

Itaconic monanilide, $\mathrm{COOH\cdot CH_2\cdot C(CH_2)\cdot CO\cdot NHPh}$, melts at 189°, and is obtained by boiling the acid with aniline and water, by allowing the solution of acid aniline itaconate to remain in the cold, as well as by Gottlieb's dry process.

Citracontolil,  $<\begin{matrix}\mathrm{CMe\cdot CO}\\\mathrm{CH-CO}\end{matrix}>\mathrm{N\cdot C_6H_4Me}$, melts at 114·5°, crystallises readily from hot water, and is insoluble in acids and alkalis. By warming the aqueous acid with paratoluidine, the acid toluide, melting at 166°, is first formed; and by recrystallisation several times from hot water is converted into the tolil. Citraconic acid seems to form anilides with orthotoluidine and α- and β-naphthylamine. It is remarkable that such a feeble base as metamidobenzoic acid forms an anil,  $<\begin{matrix}\mathrm{CMe\cdot CO}\\\mathrm{CH-CO}\end{matrix}>\mathrm{N\cdot C_6H_4\cdot COOH}$, melting at 218°. Sulphanilic acid does not react with citraconic acid, but phenylhydrazine readily yields an azide,  $\ll\begin{array}{l}\mathrm{CMe\cdot CO}\\ \mathrm{CH{-}CO}\end{array}>N_2HPh$, which forms bright yellow crystals, melting at 160°. Just as phthalic acid readily yields an anhydride, whilst its two isomerides do not, so also it yields an anil when its aniline salt is boiled with water or is allowed to stand, whilst the other two form aniline salts that are not so changed.

That the property of forming anilides on heating aqueous solutions of the aniline salts is characteristic of certain unsaturated acids, and is not shown by polybasic saturated fatty acids, is borne out by the negative results obtained from oxalic, malonic, succinic, tartaric, citric, camphoric, pyrotartaric, and mucic acids. H. B.

Nitrosotoluidines. By P. Mehne (*Ber.*, **21**, 729—735).—*Nitrosometatoluidine*, $NH_2\cdot C_6H_3Me\cdot NO$, [Me : NH : NO = 1 : 3 : 6], is prepared by heating a mixture of 1 part of nitrosometacresol, 15 parts of dry ammonium acetate, and 5 parts of ammonium chloride with constant stirring on the water-bath for about half an hour, the reaction being facilitated by the addition of some powdered ammonium carbonate from time to time. It crystallises in glistening, steel-blue, feathery needles, which are green by transmitted light, melts at 178°, and is nearly insoluble in light petroleum, soluble in water, readily soluble in alcohol, ether, hot benzene, and chloroform. It dissolves in dilute acids with yellowish-red coloration, and when heated with alkalis is reconverted into nitrosocresol with evolution of ammonia.

Nitroso-orthotoluidine, [Me : NH : NO = 1 : 2 : 5], is prepared from nitroso-orthocresol in like manner to the meta-compound. It crystallises in concentrically-grouped, globular aggregates of small, green needles with bluish reflex, and is very sparingly soluble in light petroleum, more readily in water, readily soluble in ether, alcohol, hot benzene, and chloroform. It is less stable than the meta-compound; when heated, it suffers slight decomposition at 60°, and melts at 115—116° with feeble explosion; when heated with aqueous soda, it yields ammonia and sodium nitrosophenol. When reduced with tin or zinc and hydrochloric acid, both nitrosotoluidines yield chlorinated products difficult to purify; these products were therefore oxidised with chromic acid, when in each case the same toluquinone (m. p. 70—71°) was obtained. This renders it very probable that in each the nitroso- and amido-groups are in the para-positions relatively to one another, further proof of this is obtained in the fact that both nitroso-compounds yield the same toluquinonedioxime when treated with hydroxylamine hydrochloride.

Toluquinonedioxime, [Me : NOH : NOH = 1 : 2 : 5], so obtained forms small, yellow, microscopic needles, turns brown at 210°, explodes vigorously at 234°, and is soluble in hot water, alcohol, and ether, very sparingly in benzene and chloroform, insoluble in light petroleum. When oxidised in alkaline solution, it yields 2 : 5-*dinitrosotoluene;* this is yellow, noncrystalline, turns brown at 125°, melts with slight explosion at 144°, can be sublimed, and distils readily with steam. It is probable that the last two compounds are identical with those described by Nietzki and Guitermann (this vol., p. 471).

A. J. G.

Laws of Substitution of the Aromatic Amines. By L. LIMPACH (*Ber.*, **21**, 640—642).—In this and the following investigation of the laws governing the substitution of methyl for hydrogen in the benzene-ring in aromatic amines, the methylation was effected by heating the hydrochloride of the amine with methyl alcohol in molecular proportion at 250—300° under pressure.

Aniline yields mesidine, 1 : 3 : 4-metaxylidine and paratoluidine, not even traces of either ortho- or meta-toluidine being ever observed. From this it follows that the methyl-group first takes the para-position to form paratoluidine, next by entering one of the ortho-positions, forms 1 : 3 : 4-metaxylidine, and finally by occupying the other ortho-position yields mesidine.

Ortho- and para-toluidine both yield 1 : 3 : 4-metaxylidine and mesidine. As shown by Hofmann, 1 : 3 : 4-metaxylidine yields only mesidine. Further methylation in the benzene-ring could not be effected, the hydrogen-atoms standing in the meta-position relatively to the amido-group seeming to be incapable of being displaced by alkyl-groups. The statement of Nölting and Baumann (Abstr., 1885, 893) as to the methylation of 1 : 3 : 4-metaxylidine is incorrect.

A. J. G.

Methylation of Symmetrical Metaxylidine. By L. LIMPACH (*Ber.*, **21**, 643—646).—The methylation was effected as described in the preceding Abstract. Symmetrical metaxylidine yields isocumidine, $[NH_2 : (Me)_3 = 1 : 3 : 4 : 5]$, which on further methylation yields Hofmann's pentamethylamidobenzene (Abstr., 1885, 1128), and a new tetramethylamidobenzene; these can be separated by treatment with boiling water, in which the latter alone dissolves.

Tetramethylamidobenzene, $[NH_2 : (Me)_4 = 1 : 2 : 3 : 4 : 5]$, crystallises in splendid, nacreous plates, melts at 66°, sublimes readily, boils at 259—260° (uncorr.), and then solidifies in large prisms which melt at 64°. The formyl compound crystallises in silky needles, and melts at 143—144°; the acetyl compound melts at 169·5°.

Tetramethylphenol, $C_6HMe_4{\cdot}OH$, prepared by mixing the sulphate of the base with a nitrite and heating, forms long, white needles, melts at 80—81°, boils at 248—250° (uncorr.), and can be distilled with steam.

Metatoluidine on methylation yields 1 : 2 : 4-orthoxylidine. Paraxylidine yields pseudocumidine, and this on further methylation yields the known tetramethylamidobenzene (m. p. 23—24°).

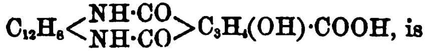
A. J. G.

Amides of Tribasic Fatty Acids. By A. SCHNEIDER (*Ber.*, **21**, 660—671).—When citric acid (1 mol.) and pseudocumidine (3 mols.) are heated for 12 hours at 160°, a mixture of tri- and di-cumidide are formed, and can be separated by boiling with alcohol, in which the dicumidide is the more soluble.

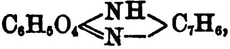
Citrotricumidide, $C_6H_5O_4(NH{\cdot}C_9H_{11})_3$, forms a white, microcrystalline powder, melts at 185°, and is sparingly soluble in alcohol, insoluble in water. When boiled with hydrochloric acid for some time, it is converted into cumidine and the dicumidide.

Citrodicumidide, $C_9H_{11}{\cdot}N{:}C_6H_5O_4{\cdot}NH{\cdot}C_9H_{11}$, forms the main product in the reaction described above, but can be obtained free from the tricumidide if only 2 mols. of pseudocumidine are employed. It crystallises in prisms, seemingly of the hexagonal system, melts at 173°, is insoluble in water and ether, readily soluble in alcohol, benzene, acetic acid, and chloroform. It is stable towards acids, but is converted by alkalis into *citrodicumidic acid*, $COOH\cdot C_5H_3O_3(NH\cdot C_9H_{11})_2$; this forms leafy crystals, melts at 194°, is insoluble in water, readily soluble in alcohol, benzene, and acetic acid. The sodium salt forms white needles, melts at 235—236°, and is very sparingly soluble in water.

Cumidine citrate, $C_6H_8O_7\cdot C_9H_{13}N$, is obtained by adding cumidine to a hot alcoholic solution of citric acid; it forms nodular crystals, melts at 132—133°, and does not yield citrocumidic acid when heated, but is resolved into its components.

Citrobenzidilic acid,  $C_{12}H_8\left\langle\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}\right\rangle C_3H_4(OH)\cdot COOH$, is prepared by heating an intimate mixture of citric acid and benzidine at 140—150° for four to five hours. It forms a white, crystalline powder, which under the microscope seems to be rhombic, begins to decompose at 260°, and carbonises at above 300° without melting, is sparingly soluble in boiling alcohol, readily in acetic acid, and is insoluble in ether, benzene, light petroleum, chloroform, and carbon bisulphide. The salts are amorphous.

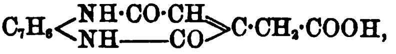
Normal benzidine citrate, $2C_6H_8O_7,3C_{12}H_{12}N_2$, is a white, amorphous powder, soluble in water, alcohol, and acetic acid.

Citrotoluylenediamide,  $C_6H_5O_4\left\langle\begin{matrix}NH\\N-\end{matrix}\right\rangle C_7H_6$, is prepared by heating citric acid and toluylenediamine (m. p. 99°) in molecular proportion for a day at 120—130°; it forms microscopic, seemingly octahedral crystals, decomposes at 187°, and can only be dissolved by very long-continued boiling with alcohol. *Normal toluylenediamine citrate* was also prepared as a slightly yellow, amorphous powder. The action of ethylenediamine on citric acid led to no useful result.

Trinitrocitrotrianil, $OH\cdot C_3H_4(CO\cdot NH\cdot C_6H_4\cdot NO_2)_3$, prepared by nitrating Pebal's citrotrianil, forms yellow, rhombic crystals, melts at 108° with decomposition, and is soluble in ether, nitrobenzene, hot alcohol, and boiling benzene. When reduced, it is converted into aniline, and other products which could not be obtained in a pure state.

When sodium citrate is heated with cyanuric chloride, it yields sodium cyanurate and citric chloride.

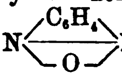
Benzidine and aconitic acid do not react at moderate temperatures, whilst at higher temperatures, mixtures are formed of such a nature as to be unworkable.

Aconitotoluylenediamic acid,  $C_7H_6\left\langle\begin{matrix}NH\cdot CO\cdot CH\\NH\text{——}CO\end{matrix}\right\rangle C\cdot CH_2\cdot COOH$, is obtained by heating a mixture of toluylenediamine and aconitic acid at 160—170°; it is a green, amorphous powder, which does not melt at 295°, is soluble in hot acetic acid, insoluble in water, alcohol, ether, and benzene, and soluble in alkalis.

Attempts to prepare the amides of aconitic acid were unsuccessful; the action of strong aqueous ammonia on ethyl citrate yields citrazinic acid.

A. J. G.

Aromatic Nitroso-bases. By L. WACKER (*Annalen*, **234**, 290—307).—*Paranitrosopropylaniline*,



$\mathrm{N}\begin{array}{c}\diagup C_6H_4 \diagdown \\ \diagdown O \diagup\end{array}\mathrm{NHPr}^{\alpha}$, is prepared by the action of alcoholic hydrogen chloride on the nitrosamine of normal propylaniline. It resembles nitrosoethylaniline in its properties, and forms steel-blue, needle-shaped crystals. It melts at 59°, and dissolves readily in alcohol, ether, and benzene. It forms crystalline salts with hydrochloric, sulphuric, oxalic, and picric acids. *Paranitrosopropylaniline-nitrosamine* melts at 69°, and dissolves in alcohol and ether. *Propylphenylenediamine* prepared from nitrosopropylaniline hydrochloride by reduction with tin and hydrochloric acid, boils at 281° without decomposition. It is soluble in alcohol, ether, and benzene, and forms a crystalline hydrochloride, $NH_2{\cdot}C_6H_4{\cdot}NHPr,2HCl$. By heating with aqueous soda, nitrosopropylaniline is decomposed into propylamine and nitrosophenol.

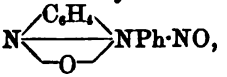
Paranitroso-isobutylaniline forms steel-blue crystals, melts at 93—94°, and forms a crystalline hydrochloride. The *nitrosamine* is soluble in alcohol, ether, and benzene. *Isebutylphenylenediamine* melts at 39°. The hydrochloride is soluble in water, but insoluble in ether. Nitroso-isobutylaniline is decomposed by boiling solutions of alkalis, yielding isobutylamine and nitrosophenol.

The preparation of nitroso-α-dinaphthylamine has been described by Fischer and Hepp (Abstr., 1887, 729). By reducing the acid solution with tin, or the alcoholic solution with ammonium sulphide, amido-α-dinaphthylamine is obtained. The nitroso-compound is decomposed by boiling with dilute sulphuric acid into α-naphthylamine and α-nitrosonaphthol.

Nitrosophenyl-α-naphthylamine under similar treatment splits up into α-nitrosonaphthol and aniline. Reduction with tin and hydrochloric acid converts it into α-amidophenylnaphthylamine. This substance must have the constitution represented by the formula $NHPh{\cdot}C_{10}H_6{\cdot}NH_2$.

W. C. W.

Nitramine from Mesidine. By E. A. KLOBBIE (*Rec. Trav. Chim.*, **6**, 31—35).—Mesitylene was added gradually to cooled nitric acid of sp. gr. 1·5, and the small quantity of trinitro-derivative formed was separated by recrystallisation from boiling alcohol. A warm saturated alcoholic solution of the nitromesitylene was heated in sealed tubes at 110—115° with a concentrated aqueous solution of ammonium sulphide, and the nitromesidine was separated from the precipitated sulphur by solution in alcohol, from which it crystallises in yellow needles melting at 73°. When treated with nitrous acid, it yields mononitromesitylene. This was reduced by means of tin and hydrochloric acid, and the mesidine thus obtained was heated in sealed tubes at 220—230° for 48 hours with methyl alcohol and hydrochloric acid in the same proportions as in the preparation of dimethylorthotoluidine (Abstr., 1879, 311). In this way, dimethylmesidine, boiling at 213—216°, is obtained, and this is dissolved in its own volume of concentrated sulphuric acid, added gradually to 10 or 12 times the weight of nitric acid of sp. gr. 1·5, boiled for a short time, poured into cold water, and the precipitate crystallised from alcohol. The product forms yellowish, opaque crystals of the composition $C_{10}H_{12}N_4O_6$, very slightly soluble in cold alcohol. The two hydrogen-atoms in mesidine have been displaced by nitroxyl-groups, and the third nitroxyl-group must either have displaced methyl from the benzene nucleus, which is improbable, or have displaced one of the methyls in the amido-group. In that case, the product is *dinitromesitylene methylnitramide*, $C_6Me_3(NO_2)_2\cdot NMeNO_2$. It melts at 137—138°, is easily soluble in benzene, ethyl acetate, and acetone, slightly soluble in ether and acetic acid, almost insoluble in light petroleum. With potash it yields no ammonia and no coloration, this result being due to the influence of the meta-position of the nitroxyl. Reduction with tin and hydrochloric acid does not yield satisfactory results; reduction with ammonium sulphide in sealed tubes at 120° yields yellow needles melting at 137°. C. H. B.

Paranitrosodiphenylamine. By M. Ikuta (*Annalen*, **243**, 272—289).—The preparation and many of the properties of paranitrosodiphenylamine have been recently described by O. Fischer and Hepp (Abstr., 1887, 244). This substance dissolves in strong solutions of alkalis, forming salts which are decomposed by carbonic anhydride, the nitrosodiphenylamine being precipitated in a pure state. The picrate is deposited from an ethereal solution in crystals. It is decomposed by boiling with alcohol or ether. The base dissolves in acetic anhydride, yielding the *acetylamine* $NPhAc\cdot C_6H_4\cdot NO$, a substance crystallising in red-coloured prisms and melting at 96—97°. It is freely soluble in ether, alcohol, and benzene. The *nitrosamine*  $N{<}\overset{C_6H_4}{\underset{O}{\longrightarrow}}{>}NPh\cdot NO$, forms yellowish-green plates soluble in benzene, alcohol, and ether. It melts at 98° with decomposition, and yields Liebermann's reaction with phenol and sulphuric acid.

Paranitrosodiphenylamine is decomposed by boiling with alkalis or dilute sulphuric acid, yielding paranitrosophenol and aniline. It is completely reduced by alcoholic potash at 150°, or more easily by the action of tin and hydrochloric acid, forming *paramidodiphenylamine*. This amido-base melts at 66° and dissolves in ether and alcohol. The sulphate is crystalline and is almost insoluble in cold water. Ferric chloride produces in the aqueous solution of the hydrochloride a red coloration which changes to green.

Diazodiphenylamine sulphate forms golden needles. It is identical with the substance Fischer and Hepp obtained by treating paranitrosodiphenylamine with excess of sodium nitrite and dilute sulphuric acid. The relation between azophenine and nitrosodiphenylamine has already been discussed by Fischer and Hepp (Abstr., 1887, 1105).

The sulphate of diazodiphenylamine is converted into *parachlorodiphenylamine* by treatment with a 10 per cent. cuprous chloride solution. This is a feeble base. It melts at 74°, and dissolves freely in ether, alcohol, benzene, methyl alcohol, and light petroleum. The *nitrosamine*, $NO\cdot NPh\cdot C_6H_4Cl$, forms four-sided plates, melts at 88°, and dissolves freely in alcohol and ether. The ethereal solution deposits crystals of paranitrosochlorodiphenylamine hydrochloride on the cautious addition of alcoholic hydrogen chloride.

Paranitrosochlorodiphenylamine melts at 158—159°, and crystallises in plates. It dissolves in alcohol, ether, chloroform, and benzene, also in sulphuric acid with a carmine coloration. When treated with aniline hydrochloride and aniline, it yields an azophenine-derivative melting at 230°. W. C. W.

Action of Catechol on Alkylenediamines. By C. Ris (*Ber.*, **21**, 378—386; compare Abstr., 1887, 722).—*Ethyleneorthophenylenediamine hydrochloride*, $2C_8H_{10}N_2,3HCl$, crystallises in colourless, lustrous scales, melts at 150° with decomposition, and is readily soluble in water and alcohol. The *acetyl*-derivative, $C_8H_8N_2Ac_2$, crystallises in small, white granules, melts at 144°, boils with partial decomposition at 350° and is readily soluble in hot water, alcohol, benzene, and chloroform, sparingly soluble in ether at the boiling point. When heated with excess of methyl iodide and methyl alcohol for six hours at 100—110°, the base is converted into the *methiodide* of *dimethylethylene-orthophenylenediamine*, $C_8H_8N_2Me_2,MeI$, which crystallises from a dilute alcoholic solution in compact, colourless scales, melts above 200° with decomposition, is readily soluble in hot water and alcohol, sparingly soluble in benzene and ether, and is not decomposed by heating with aqueous soda or hydrochloric acid. On treatment in aqueous solution with silver oxide, it is converted into the ammonium-base, which forms a syrupy liquid having a strongly alkaline reaction, and yields a *platinochloride*,

$$(C_8H_8N_2Me_2,MeCl)_2PtCl_4,$$

crystallising in small, lustrous, yellow scales. If, however, ethylene-orthophenylenediamine is heated with methyl iodide alone at 100—110°, the *methyl*-derivative, $C_8H_9N_2Me$, is the sole product. It is a bright-yellow oil, which boils for the most part at 273—275°, is miscible with the ordinary organic solvents, and gives a pure blue colour on treatment with ferric chloride. This compound is also formed during the evaporation of the solution of the ammonium-base of the dimethyl-derivative, and can be obtained, together with ammonia, methylamine, carbon, and methyl iodide by the dry distillation of the corresponding methiodide.

Propylene-orthophenylenediamine, $C_6H_4<\substack{NH\\NH}>C_2H_3\cdot Me$, is formed when 1 gram of catechol is heated with 2·6 grams of propylenediamine at 200° for seven hours. It crystallises from light petroleum in colourless, lustrous scales, melts at 72°, boils at 283—284°, and is readily soluble in alcohol, benzene, chloroform, and hot water. The aqueous solution is coloured a pure blue by ferric chloride and the colour changes to green, yellowish-green, and finally reddish-brown on addition of much hydrochloric acid; the resulting solution, however, regains its original blue colour on boiling or on dilution with water. The *hydrochloride*, $2C_9H_{12}N_2,3HCl$, is a pale rose-coloured, crystalline powder readily soluble in water and alcohol; the *picrate*, $3C_9H_{12}N_2,2C_6H_2(NO_2)_3\cdot OH$, crystallises in slender, sulphur-yellow needles, decomposes at 160—161° with the evolution of gas, and is soluble in benzene. W. P. W.

Aromatic Nitroso-bases. By E. Kock (*Annalen*, **243**, 307—313).—*Ethylorthotoluylenediamine* is prepared by the reduction of the paranitroso-ethylorthotoluidine described by Fischer and Hepp (Abstr., 1887, 244). It is a liquid boiling at 264 (corr.) and miscible with ether. The hydrochloride melts at 124° with decomposition; it is crystalline and deliquescent. *Paranitrosomethylorthotoluidine*, $C_8H_{10}N_2O$ (from orthotolylmethylnitrosamine), forms green plates. It melts at 151° and is decomposed by sodium hydroxide, yielding methylamine and paranitroso-orthocresol. Oxidation with potassium permanganate converts it into paranitromethylorthotoluidine. The nitro-product forms greenish-yellow needles and melts at 134°.

Paranitroso-α-naphthylethylamine dissolves in benzene, alcohol, and chloroform, and melts with decomposition at 133°. The hydrochloride, $C_{12}H_{12}N_2O,HCl$, is sparingly soluble in dilute hydrochloric acid. The picrate melts with decomposition at 174°. The sodium salt, $C_{12}H_{13}N_2O_2Na$, forms white scales soluble in water and alcohol, forming orange-coloured liquids. The base is decomposed by sodium hydroxide into nitroso-α-naphthol and ethylamine, and by reduction with tin and hydrochloric acid is converted into *ethyl-α-naphthylenediamine hydrochloride*. This salt melts at 152°. The picrate melts at 180°, and is deposited from a hot aqueous solution in needles. The diamine has not been isolated. W. C. W.

Relation between Hydrazides and Azo-compounds. By A. Bernthsen (*Ber.*, **21**, 743—745).—The author points out that the peculiar properties of the compound of phenylhydrazine with acridylaldehyde (Abstr., 1887, 859) would seem to be due to another of those changes from hydrazines to azo-compounds to which attention was first called by the work of Japp and Klingemann (*Ber.*, **20**, 2942, 3284, 3398). A. J. G.

Nitrocymene and Azocymene. By G. Shumoff (*J. Russ. Chem. Soc.*, 1887, 118—122).—Cymene, prepared partly by the action of phosphorus sulphide on camphor, partly from cumin oil, is dissolved in glacial acetic acid, and to the solution, cooled with ice and snow, a mixture of nitric acid of sp. gr. 1·52 is added. After addition of water, the nitrocymene is extracted with ether and reduced by means of sodium amalgam. The azocymene obtained in this way forms ruby-coloured plates, melts at 86°, is easily soluble in benzene, less so in alcohol. It is soluble without alteration in sulphuric and acetic acids, but insoluble in hydrochloric acid.

Zutkowsky finds that the crystals are rhombic: $a : b : c = 0·978284 : 1 : 1·567289$. The principal forms are the basic pyramid (111) and the pinacoid (001). B. B.

Orthamidoazo-compounds of Xylene and Pseudocumene. By T. Zincke and H. Jaenke (*Ber.*, **21**, 540—548).—Orthamidoazoxylene can be diazotised in presence of excess of acid in alcoholic solution by nitrous acid or sodium nitrite.

The *hydrochloride* of the diazo-compound forms small, reddish-brown needles; the *nitrate* crystallises in wide needles rather sparingly soluble. The *sulphate* forms almost brick-red needles. When the salts are heated with alcohol, an azo-compound is formed identical with that obtained by oxidising the diazohydride. The *diazoperbromide*, $C_{16}H_{17}N_4Br_3$, crystallises in blood-coloured needles which melt with decomposition at 127—129°.

The *diazo-imide*, $C_{16}H_{17}N_5$, is prepared by the action of alcoholic ammonia on the dry perbromide in presence of much ether, and crystallises from light petroleum in stellate groups of thick, red needles readily soluble in ether; it melts at 77°, decomposes at 85°, and detonates when quickly heated.

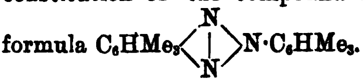
The *diazohydride*, $C_{16}H_{18}N_4$, is obtained in a manner similar to the tolyl-compound. It forms small, yellowish, monoclinic prisms, melts at 136—137°, is insoluble in water, readily soluble in acetic acid and benzene, and in its behaviour resembles that of the diazohydride from orthamidoazotoluene (Abstr., 1886, 795). Nitric acid converts it into the diazo-nitrate, and silver oxide converts it into azoxylene.

Metapara-azoxylene, $C_{16}H_{18}N_2$ [Me : Me : N : N : Me : Me = 1 : 2 : 4 : 5 : 1 : 3], is prepared from the diazo-salts of orthamidoazoxylene or from the diazohydride. The yield is small and the purification difficult. It crystallises from alcohol in small, bright-red plates which melt at 46—47°, and is readily soluble.

When a cooled solution of orthamido-azoxylene in 20 parts of glacial acetic acid is treated with an excess of a concentrated solution of potassium dichromate, and the solution, after some hours, precipitated with water, the compound $C_{16}H_{17}N_3$ is obtained. This crystallises in yellowish, monoclinic prisms melting at 83—85°. The compound is also formed when the diazoamide, $C_{16}H_{17}N_5$, is boiled in alcoholic solution.

The *diazo*-compound of orthamidopseudocumene is best prepared by passing nitrous anhydride into the solution of the latter compound in glacial acetic acid. The *perbromide* forms a dark-red crystalline precipitate melting at 122—124° with decomposition. The *diazo-imide*, $C_{18}H_{21}N_5$, prepared from the perbromide crystallises in thick, red needles which melt at 90—91° with decomposition and detonate when quickly heated. When the solution of the diazo-imide in glacial acetic acid is heated, the compound $C_{18}H_{21}N_3$ is formed.

The *diazo-hydride*, $C_{18}H_{22}N_4$, prepared by reducing the diazochloride with stannous chloride, crystallises from alcohol in small, lustrous, almost colourless, hexagonal plates melting at 151—153°; it dissolves rather readily in hot alcohol, glacial acetic acid and benzene, sparingly in ether and light petroleum. The compound $C_{18}H_{21}N_3$ is also formed when orthamidopseudocumene is dissolved in 20 parts of glacial acetic acid and a slight excess of concentrated solution of potassium dichromate added in drops. It is afterwards precipitated with water and crystallised from glacial acetic acid and then from methyl alcohol. It forms large, lustrous, whitish plates which melt at 83—85°. The constitution of the compound is provisionally represented by the formula



$$C_6HMe_3\left\langle\overset{N}{\underset{N}{|}}\right\rangle N\cdot C_6HMe_3.$$

N. H. M.

Quinonedioximes. By R. Nietzki and A. L. Guitermann (*Ber.*, **21**, 428—434; compare Abstr., 1887, 575).—The most convenient method of preparing quinonedioxime (*loc. cit.*) is by the action of hydroxylamine on nitrosophenol. It crystallises in two modifications, probably differing in the amount of water they contain, namely, short, colourless needles, and long, slender, yellow needles which fall to a colourless powder on drying. Although, like all other paradioximes, it resembles the orthodioximes in general behaviour, yet it is sharply distinguished from the latter by its not forming an anhydro-compound; thus when heated with acetic anhydride it yields the diacetyl compound, $C_6H_4(NOAc)_2$, which forms colourless needles and is sparingly soluble in water and ether, more readily in alcohol, very readily in acetic acid. The paradioximes and the dinitroso-compounds derived from them, when treated with concentrated nitric acid, are converted into the corresponding dinitro-derivatives; with quinonedioxime this furnishes the most convenient method of preparing paradinitrobenzene.

Toluquinonedioxime is best prepared by suspending nitroso-orthocresol in 50 to 60 parts of water, adding the calculated amount of hydroxylamine, and heating for 10 hours at 60—70°; it is also formed, although not so readily, from the meta-compound. It forms yellow needles, which become colourless on drying, explodes at 220° without melting, and on filtration becomes strongly electrical. The *diacetyl* compound crystallises in colourless needles, and melts at 120°. When oxidised with potassium ferricyanide in alkaline solution, it yields *dinitrosotoluene;* this compound, $C_7H_6(NO)_2$, has only been obtained as an amorphous, yellow powder, is insoluble in all solvents except acetic acid, and is far more volatile than dinitrosobenzene; it sublimes markedly at 100°, and distils with steam—although with partial decomposition; it melts at 133°.

Paradinitrotoluene [Me : NO : NH = 1 : 2 : 5] is obtained by treating toluquinonedioxime or the dinitroso-compound with fuming nitric acid; it forms tufts of pale-yellow, moderately thick needles, and melts at 48°.

α-Naphthaquinonedioxime, $C_{10}H_6(NOH)_2$, is prepared by suspending 5 grams of α-nitroso-α-naphthol in 500 c.c. of water, adding the necessary quantity of hydroxylamine hydrochloride and then so much alcohol that all dissolves on warming; the whole is then heated for two days in a reflux apparatus. It forms slender, colourless needles melting at 207° with decomposition, and yields an acetyl-derivative which crystallises in colourless, interlaced needles, and melts at 160°. It yields paradiamidonaphthalene on reduction, and, when oxidised with potassium ferricyanide in alkaline solution, is converted into 1 : 4-*dinitrosonaphthalene;* this forms a yellow, non-volatile powder, insoluble in all indifferent solvents; it explodes at 120°.

A. J. G.

Manufacture of Rosaniline by the Arsenic Acid Process. By O. MÜHLHÄUSER (*Dingl. polyt. J.*, **266**, 455—467, 503—517, and 547—563).—The preparation of rosaniline by heating aniline with arsenic acid was patented almost simultaneously by Medlock and Nicholson in 1860. In the same year Girard and de Laire patented the process in France, whilst, in 1864, Dawson obtained a patent according to which the dye was prepared by heating aniline under pressure with an aqueous solution of arsenic acid. The proportions of aniline and arsenic acid used by different manufacturers have varied very much; that now used which is found to give the best results is 1 mol. of arsenic acid, As_2O_5, to 2 mols. of aniline. This mixture is heated in vertical cast-iron boilers provided with stirrers. The charge consists of 570 kilos. of syrupy arsenic acid of 74° B. and 340 kilos. of aniline oil of 1·008 sp. gr. It is heated gradually to about 120°, then more rapidly to 180°, after which the temperature is regulated so that the melt is finished during the next two hours, the final temperature being 185—189°. The crude melt contains the following ingredients:—Arsenious acid, arsenic acid, pararosaniline, methylpararosaniline, dimethylpararosaniline, chrysaniline, methylchrysaniline, violaniline, mauvaniline, brown colouring matters, and humus-like substances of unknown composition. Phenylated substances are formed when the quantity of aniline exceeds the proportion of 2 mols. to 1 mol. of arsenic acid. The oil mostly used has a sp. gr. of 1·008, distils between 190° and 198°, and is obtained by mixing 1 part of aniline with 2 parts of commercial toluidine. As the latter always contains 36 per cent. of paratoluidine and about 64 per cent. of orthotoluidine, the composition of the aniline oil is 33·3 per cent. of aniline, 24 per cent. of paratoluidine, and 42·7 per cent. of orthotoluidine.

The crude melt is allowed to cool, broken up roughly, and boiled up with water. The liquor is run into crystallising tanks in which it is treated with hydrochloric acid and salt. On standing, the crude rosaniline crystallises out; this is purified by recrystallisation. The different operations are described in detail in the original paper. The author also gives a minute account of the preparation of rosaniline base and of "cerise." He also discusses the working up of the crystallisation residues, the preparation of maroon, and the treatment of residues. D. B.

Azophenine and Quinonanilide. By O. FISCHER and E. HEPP (*Ber.*, **21**, 676—684).—The anilidoethoxyquinonanilide described by Zincke and v. Hagen (Abstr., 1885, 787) is obtained when 1 part of azophenine is heated with 100 parts of alcohol and 5 parts of sulphuric acid for one hour, at a temperature not exceeding 70°; it melts at 137°. If methyl alcohol is substituted for ethyl alcohol, the corresponding methoxy-compound, melting at 194°, is obtained. The melting points given by Zincke and v. Hagen are rather low.

When azophenine is boiled with stannous chloride and acetic acid, it is reduced to a colourless, crystalline substance, stable in acid solution, but converted by ammonia into a red base which yields blue salts.

Trichlorazophenine, $C_{30}H_{21}Cl_3N_4$, is prepared by adding 1 part of nitrosodiphenylamine in small portions to a mixture of 1 part of parachloraniline hydrochloride and 5 parts of parachloraniline heated at 70°; it forms brownish-red prisms, melts at 246°, and is soluble in alcohol. A different substance is obtained by the action of nitrosophenol on parachloraniline; it forms red prisms, melts at 265°, is insoluble in alcohol, sparingly soluble in benzene, and, although not obtained quite pure, seems to be *tetrachlorazophenine*, $C_{30}H_{20}N_4Cl_4$.

By the action of nitroso-orthocresol on aniline, Zincke and v. Hagen's dianilidotoluquinonanilide (Abstr., 1883, 1118) is formed; it melts at 172—173° (not 167°). *Diparatoluidotoluquinone-paratoluidide*, $C_{28}H_{29}N_3O$, is prepared in like manner from nitroso-orthocresol and paratoluidine; it crystallises in Bordeaux-red plates and melts at 191°.

The authors confirm Bröme's statement (this vol., p. 491) that all three nitroso-naphthols yield the same anilidoquinonanilide. This substance is also formed from benzeneazo-α-naphthol with aniline and aniline hydrochloride at 100°, from benzeneazo-α-naphthylamine, from nitroso-phenyl-α-naphthylamine, from benzeneazoethyl-α-naphthylamine, and from benzeneazophenyl-α-naphthylamine. In the last processes, a considerable quantity of a white, crystalline substance melting at 191°, of the formula $C_{34}H_{28}N_4$, but of unknown constitution is obtained; it is formed in smaller amount by the action of all nitroso-naphthols on aniline. Anilidonaphthaquinonanilide, from whatever source prepared, yields hydroxynaphthaquinone and aniline when heated with moderately concentrated sulphuric acid. When reduced with zinc-dust in acid solution, it gives aniline and naphthalene.

Dibromanilidonaphthaquinonanilide, $C_{22}H_{14}Br_2N_2O$, is prepared from α-nitroso-α- or β-naphthol by fusion with parabromaniline and parabromaniline hydrochloride; it forms long, red, interlaced needles, melts at 235°, and is very sparingly soluble in alcohol, more readily in benzene. The corresponding *dichloro*-compound melts at 217—218°.

On the whole, the authors consider that azophenine is better represented by the formula $C_{30}H_{24}N_4$ than by $C_{36}H_{29}N_5$, that proposed by Witt and adopted by the authors in their previous paper (Abstr., 1887, 1105). There can be no doubt of the intimate relation existing between azophenine and quinonanilide, and in confirmation of this it is now shown that if in preparing induline by heating quinonanilide with aniline and aniline hydrochloride at 170°, the experiment is stopped as soon as the melt begins to turn blue, azophenine is contained in the product. A. J. G.

Action of Chloracetone on Diphenylthiocarbamide. By B. PAWLEWSKI (*Ber.*, **21**, 401—405).—*Acetonyldiphenylthiocarbamide*, NHPh·CS·NPh·CH₂·COMe, is obtained, as its hydrochloride, by the action of chloracetone on diphenylthiocarbamide. It crystallises in long, pale-yellow prisms, melts at 139—140° (uncorr.), resolidifies at 110—112°, and is insoluble in water, sparingly soluble in cold alcohol. The *hydrochloride*, $C_{16}H_{16}SN_2O,HCl$, crystallises in long, quadratic needles and melts at 230—232° (uncorr.); the *platinochloride*, $(C_{16}H_{16}SN_2O)_2,H_2PtCl_6$, is insoluble in water and alcohol.

Ethyl chlorocarbonate and thiocarbamide react to form a compound, $NH_2{\cdot}CS{\cdot}NH{\cdot}COOEt,HCl$, which melts at 117°. Chloracetone and thiocarbamide yield a substance of the formula

$$NH_2{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}COMe,HCl,$$

melting at 126°. Similar reactions are being investigated.

A. J. G.

Substituted Biurets. By B. Kühn and E. Henschel (*Ber.*, **21**, 504—506).—Triphenylbiuret is formed when diphenylcarbamide is dissolved in an excess of hot phenyl cyanate, and the whole heated for half to one hour at 150°; at a higher temperature, it decomposes into diphenylcarbamide and phenyl cyanate. Diphenylbiuret prepared from monophenylcarbamide melts at 208—210°.

Phenylparaditolylbiuret, $C_{22}H_{21}N_3O_2$, melts at 140°.

Phenylbenzylparatolylbiuret, $C_{22}H_{21}N_3O_2$, crystallises from dilute alcohol in microscopic needles melting at 95—104°.

Paratritolylbiuret, $C_{23}H_{23}N_3O_2$, melts at 155—156°.

Orthoparaditolylbiuret, $C_{16}H_{17}N_3O_4$, is prepared from paratolylcarbamide and paratolyl cyanate, and crystallises from dilute alcohol in white needles which melt between 216° and 224°.

Diphenylparatolylbiuret, $C_{21}H_{19}N_3O_2$, melts at 214—216°.

N. H. M.

Derivatives of Ortho-xylene. By H. Strassmann (*Ber.*, **21**, 576—581).—*Ortho-xylylphthalimide*, $C_6H_4Me{\cdot}CH_2{\cdot}N{:}C_8H_4O_2$, is obtained by heating ortho-xylyl bromide and potassium phthalimide at 200° for half an hour; the product crystallises from alcohol in white, hexagonal forms, melting at 148—149°; the yield is 76 per cent. of the theoretical amount.

Ortho-xylylphthalamic acid, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_8H_9$, is produced when the preceding compound is boiled with soda; it melts at 156°, and crystallises from alcohol in needles.

Ortho-xylylamine hydrochloride is formed when xylylphthalimide is heated in sealed tubes with hydrochloric acid; the product crystallises from alcohol in transparent needles, and when treated with alkalis yields *ortho-xylylamine*, $C_6H_4Me{\cdot}CH_2{\cdot}NH_2$, which is a colourless liquid boiling at 202°. The *platinochloride*, $(C_8H_{11}N)_2,H_2PtCl_6$, crystallises in yellow needles, the *sulphate* in prisms, readily soluble in water, and the *picrate*, $C_8H_{11}N_3,C_6H_3N_3O_7$, in long, yellow needles, which decompose above 170° without melting.

Ortho-xylylthiocarbamide, $NH_2{\cdot}CS{\cdot}NH{\cdot}C_8H_9$, is obtained by dissolving equivalent weights of ortho-xylylamine hydrochloride and potassium thiocyanate, and heating the residue obtained on evaporation at 140° for some time. It crystallises from water in white needles, melting at 167°, and turning red on exposure to the air.

Ortho-xylylcarbamide, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_8H_9$, is prepared in a similar manner from the sulphate of the base and potassium cyanate; it crystallises from alcohol in radiating moss-like forms, melting at 172—173°.

Ortho-xylylacetamide, $C_8H_9{\cdot}NHAc$, is formed when the hydrochloride is heated with sodium acetate and acetic anhydride; it crystallises from alcohol in needles melting at 69°.

Ortho-xylylthiocarbimide, $CSN\cdot C_8H_9$, is produced when an ethereal solution of the base is mixed with carbon bisulphide, and then distilled with mercuric chloride; it is an oil, boiling at 256°, and smelling strongly of radishes.

Ortho-xylylenediphthalimide, $C_6H_4(CH_2\cdot N\colon C_8H_4O_2)_2$, is obtained in almost theoretical quantities by gradually heating an intimate mixture of xylylene bromide and potassium phthalimide to 200°; it crystallises from acetic acid in slender, white needles melting at 253°.

Ortho-xylylenediamine hydrochloride is formed when the preceding compound is heated with hydrochloric acid at 200° for two hours; when treated with potash, it yields the free base.

Ortho-xylylenediamine, $C_6H_4(CH_2\cdot NH_2)_2$, is a strongly alkaline liquid with an ammoniacal smell, and attracts carbonic acid from the air; it gives a yellowish-red precipitate with ferric chloride, and yields the salt, $C_8H_{14}N_2Au_2Cl_8$, in yellow plates, when precipitated with auric chloride. The *picrate*, $C_6H_4(CH_2\cdot NH_2,C_6H_3N_3O_7)_2$, crystallises in yellow needles, which decompose above 170° without melting.

Orthodiacetylxylylenediamine, $C_8H_8(NHAc)_2$, crystallises in tufts of needles and melts at 146°. *Orthodibenzoylxylylenediamine*,

$$C_8H_8(NHBz)_2,$$

obtained by heating the hydrochloride with benzoic chloride at 200°, crystallises in needles melting at 168°.

Chloro-xylylenephthalimide, $CH_2Cl\cdot C_6H_4\cdot CH_2\cdot N\colon C_8H_4O_2$, is prepared by heating xylylene chloride (1 mol.) with potassium phthalimide 1 mol.); it crystallises from alcohol in prisms, melting at 140°, and when heated with hydrochloric acid yields *chloro-xylylamine hydrochloride*, $CH_2Cl\cdot C_6H_4\cdot CH_2\cdot NH_2,HCl$. F. S. K.

Tetrabenzylphosphonium - compounds. By B. Ledermann (*Ber.*, **21**, 405—409).—*Tetrabenzylphosphonium iodide*, $P(C_7H_7)_4I$, is prepared by heating phosphonium iodide (1 mol.) and benzyl alcohol (3 mols.) in sealed tubes at 100° for six to eight hours; it crystallises well, melts at 191°, and is sparingly soluble in water, more readily in chloroform, ether, and alcohol. The *chloride*, $P(C_7H_7)_4Cl$, prepared by digesting the iodide with silver chloride, forms white crystals. The *sulphate*, $(PC_{28}H_{28})_4SO_4$, also forms white crystals. The *platinochloride*, $(PC_{28}H_{28})_2PtCl_6$, is obtained as a yellow, crystalline precipitate. The *nitrate* and *bromide* both form white crystals. The *picrate* forms yellow crystals. The *mercurochloride*, $P(C_7H_7)_4HgCl_3 + H_2O$, and stannochloride $(PC_{28}H_{28})_4SnCl_6$, are insoluble. The hydroxide could not be formed, as moist silver oxide is without action on the haloïd salts, and the sulphate, when treated with barium hydroxide, yields tribenzylphosphine oxide. When tetrabenzylphosphonium iodide is boiled for some time with strong alkalis, tribenzylphosphine oxide and toluene are formed.

The oxygen in tribenzylphosphine oxide is so firmly combined that it is not displaced by treatment with phosphoric chloride or potassium hydrosulphide. Experiments made with a view to isolate tribenzylphosphine were unsuccessful. A. J. G.

Conversion of Ketones and Aldehydes into Acids and Acid Amides by Means of Ammonium Sulphide. By C. WILLGERODT (*Ber.*, **21**, 534—536).—The compounds formed by the action of ammonium sulphide on methyl aromatic ketones are not ketone-imides (Abstr., 1887, 1046) but acid amides, accompanied with the ammonium salts of the corresponding acids. Phenyl methyl ketone yielded phenylacetamide and phenylacetic acid; paratolyl methyl ketone, paratolylacetamide (m. p. 185°), and paratolylacetic acid (m. p. 92°), &c.

Aromatic ethyl and propyl ketones react similarly with ammonium sulphide. In the case of paratolyl ethyl ketone, the reaction takes place at 250°. From α-naphthyl ethyl ketone and α-naphthyl propyl ketone, the *compounds* $C_{13}H_{13}NO$ and $C_{14}H_{15}NO$, melting respectively at 140° (uncorr.) and at 160°, were obtained.

When benzil is heated with ammonium sulphide at 270°, benzoic acid and a compound melting at 241° are formed. Œnanthaldehyde and ammonium sulphide when heated at 300° yield œnanthylamide, melting at 95°; benzaldehyde reacts much more readily, and yields more benzoic acid than benzamide. N. H. M.

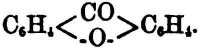
Perkin's Reaction. By H. W. SALOMONSON (*Rec. Trav. Chim.*, **6**, 23—30).—Benzaldehyde, ethyl succinate, and acetic anhydride were heated together at 125°, 140°, 180°, and 200° for six hours, but no reaction took place. Nitrobenzaldehyde and sodium succinate were heated together under various conditions but without the presence of acetic anhydride; no reaction took place. Meta- or para-nitrobenzaldehyde heated at 180—200° with sodium succinate and glacial acetic acid yields a small quantity of nitrocinnamic acid, but no nitrophenylparaconic acid.

It follows that ethyl succinate cannot be substituted for sodium succinate, or acetic acid for acetic anhydride, and it would seem that the reaction depends on the simultaneous presence of a sodium salt and an anhydride. Perkin showed that even at 100° sodium succinate is decomposed by acetic anhydride, with formation of sodium acetate and succinic anhydride, but the author finds that this reaction takes place only to a very limited extent, and there is little doubt that a condition of equilibrium is established between sodium succinate, acetic anhydride, sodium acetate and succinic anhydride. When one of these substances is removed by the action of the aldehyde, a further quantity of the same substance is formed, which is again removed by the aldehyde, and so on.

The assumption that the action takes place between the sodium salt and the aldehyde will not explain why acetic acid cannot be substituted for acetic anhydride, or ethyl succinate for sodium succinate, but these facts are explained at once, if it is assumed that the action takes place between the aldehyde and succinic anhydride. The acetic anhydride liberates a small quantity of succinic anhydride from the sodium salt with formation of sodium acetate, and as fast as the succinic anhydride reacts with the aldehyde, a fresh quantity is liberated in the nascent state until decomposition is complete. The advantage gained by using acetic anhydride in place of the anhydride corresponding with the sodium salt is due to the fact that in the latter case the anhydride is in the free state from the beginning, and is not liberated in the nascent condition during the reaction. Acetic anhydride and ethyl succinate do not interact, and the avidity of the aldehyde for the ethyl succinate is not sufficient to produce direct action.

Sodium propionate and the sodium salts of bibasic acids of the paraffin series react directly with benzaldehyde.

Perkin's reaction is strictly analogous to the aldol reaction of Wurtz. C. H. B.

Phenylsalicylic Acid and Diphenyleneketone Oxide. By C. Graebe (*Ber.*, **21**, 501—504).—*Phenylsalicylic acid*, $OPh\cdot C_6H_4\cdot COOH$, is prepared by adding the calculated amount of sodium in small pieces to phenyl salicylate, heated at 280—300° : when cold, the product is treated with alcohol, extracted with water, filtered, and precipitated with hydrochloric acid. The precipitate is redissolved in sodium carbonate, precipitated and crystallised from dilute alcohol, from which it separates in plates melting at 113°. It is readily soluble in alcohol and ether, and distils at 355° with slight decomposition into diphenylene-*a*-ketone oxide. The *silver salt* is sparingly soluble. The *methyl salt* is insoluble in alkalis. When the acid is heated with 10 parts of sulphuric acid, it is converted almost quantitatively into diphenyleneketone oxide; the constitution of the latter compound is therefore  $C_6H_4{<}\begin{smallmatrix}CO\\-O-\end{smallmatrix}{>}C_6H_4$. N. H. M.

Paramethoxyphenylacrylic Acid. By A. Einhorn and J. P. Grabfield (*Annalen*, **243**, 362—378).—*Paramethoxyphenylacryl methyl ketone*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot COMe$, is prepared by agitating a mixture of anisaldehyde, acetone, and a solution of sodium hydroxide. The compound melts at 73°, and dissolves freely in ether, alcohol, benzene, and acetic acid. It is converted into paramethoxyphenylacrylic acid (described by Perkin, this Journal, 1877, i, 408) by treatment with sodium hypochlorite. When the methyl ketone is poured into a mixture of sulphuric and nitric acids at 0°, a *nitro-derivative*, $OMe\cdot C_6H_3(NO_2)\cdot CH{:}CH\cdot COMe$, and other products are formed; this is soluble in water, alcohol, ether, ethyl acetate, and benzene, yields metanitroanisic acid on oxidation with potassium permanganate, and can also be prepared by agitating a mixture of metanitroparamethoxybenzaldehyde and acetone with an aqueous solution of sodium hydroxide.

By the nitration of paramethoxyphenylacrylic acid, metanitroparamethoxyphenylacrylic acid and *metanitroparamethoxyphenylethylene* are formed. The latter, $OMe\cdot C_6H_3(NO_2)\cdot CH{:}CH_2$, forms rhombic crystals and melts at 89°. It is volatile in a current of steam, and is soluble in the ordinary solvents. It unites directly with two atoms of bromine forming a crystalline dibromide melting at 78—79°.

Dinitroparamethoxyphenylethylene can be separated from the mononitro-product by its insolubility in chloroform. The dinitro-compound melts at 162—163°, and is deposited from alcohol in needles. It forms an additive compound with bromine. *Metanitroparamethoxybenzaldehyde* crystallises in yellow prisms, and melts at 83·5°. It is soluble in the usual solvents, and forms a compound with phenylhydrazine, melting at 130·5°. It is converted by Perkin's reaction into *metanitroparamethoxycinnamic acid.* This melts at 140°, and dissolves in ether, hot water, and alcohol. The methyl salt melts at 125°. Nitromethoxycinnamic acid does not form an additive compound with hydrobromic acid, but by the action of an ethereal solution of hydrogen bromide on the acid at 90°, ethyl bromide and ethyl nitromethoxyphenylacrylate are produced. The ethyl salt melts at 100°. At 100°, an acetic acid solution of hydrogen bromide converts nitromethoxyphenylacrylic acid into *metanitroparahydroxyphenylacrylic acid;* this crystallises in needles, melts at 198°, does not unite with hydrogen bromide, but unites with bromine (in ethereal solution) to form a dibromide. Nitromethoxycinnamic acid readily absorbs bromine forming *metanitroparamethoxyphenyldibromopropionic acid*, $OMe\cdot C_6H_3(NO_2)\cdot CHBr\cdot CHBr\cdot COOH$, which melts at 178°, and is decomposed by a cold solution of potassium hydroxide, losing 1 mol. HBr and yielding nitromethoxyphenylbromacrylic acid. Alcoholic potassium hydroxide removes 2 mols. HBr, and converts the dibromide into metanitroparamethoxyphenylpropiolic acid. W. C. W.

Compounds of Aldehydes, Ketones, and Ketonic Acids with Thioglycollic Acid. By J. BONGARTZ (*Ber.*, **21**, 478—487).—*Ethylidenedithioglycollic acid*, $CHMe(S\cdot CH_2\cdot COOH)_2$, is formed when acetaldehyde is mixed with thioglycollic acid; the product when kept in a vacuum crystallises to a white mass, which can be recrystallised from chloroform. It melts at 107—108°.

Benzylidenedithioglycollic acid, $CHPh(S\cdot CH_2\cdot COOH)_2$, crystallises from hot water (20 to 30 parts) in well-formed needles, melting at 123—124°.

Orthonitrobenzylidenedithioglycollic acid,

$$NO_2\cdot C_6H_4\cdot CH(S\cdot CH_2\cdot COOH)_2,$$

crystallises from hot chloroform in colourless crystals which gradually become yellow when exposed to light, and melt at 122—123°. The *meta-compound* crystallises from 10 per cent. acetic acid in needles, melting at 129—130°. The *para-derivative* crystallises from dilute acetic acid in lustrous, yellowish needles, melting at 161—162°.

Orthohydroxybenzylidenedithioglycollic acid,

$$OH\cdot C_6H_4\cdot CH(S\cdot CH_2\cdot COOH)_2,$$

is prepared by treating a mixture of salicylaldehyde and thioglycollic acid with zinc chloride; it is readily soluble in hot water, alcohol, and ether, insoluble in benzene, light petroleum, and chloroform, and melts at 147—148°.

Cinnamaldehydedithioglycollic acid, $CHPh:CH\cdot CH(S\cdot CH_2\cdot COOH)_2$, crystallises from hot water in white plates, melting at 142—143°, and when reduced with zinc-dust in alkaline solution yields the *compound* CHPh:CH·CH_2·S·CH_2·COOH; this crystallises in plates of a silky lustre, melting at 76—77°.

Furfuraldehydedithioglycollic acid, C_4H_3O·CH(S·CH_2·$COOH)_2$, melts at 104—105° with decomposition; it could not be obtained quite pure.

Dimethylmethylenedithioglycollic acid, CMe_2(S·CH_2·$COOH)_2$, separates from chloroform in clear crystals, melting at 126—127°.

Methylphenylmethylenedithioglycollic acid, CMePh(S·CH_2·$COOH)_2$, crystallises from water in colourless needles, melting at 135—136°.

Diphenylmethylenedithioglycollic acid, CPh_2(S·CH_2·$COOH)_2$, is obtained by heating benzophenone and thioglycollic acid with zinc chloride for several hours, and crystallises from hot dilute acetic acid in colourless needles, which melt at 175—176° with evolution of carbonic anhydride.

The additive compounds of pyruvic and thioglycollic acids have already been described (Abstr., 1886, 938).

Ethyl acetoacetate dithioglycollic acid,

$$COOEt·CH_2·CMe(S·CH_2·COOH)_2,$$

is prepared by passing dry hydrogen chloride through a mixture of ethyl acetoacetate and thioglycollic acid; it forms a white, crystalline powder, readily soluble in warm water and cold alcohol, almost insoluble in light petroleum, and melts at 95—96°.

Levulodithioglycollic acid,

$$COOH·CH_2·CH_2·CMe(S·CH_2·COOH)_2,$$

crystallises from water in needles melting at 153—154°, and is very stable towards alkalis.

When a dilute aqueous solution of benzylidenedithioglycollic acid (2 grams) is shaken with a solution of 4 grams of potassium permanganate in 1 litre of water, the *disulphone*, CHPh($SO_2Me)_2$, is formed. This crystallises in slender needles, melting at 162—163°, readily soluble in hot water, sparingly soluble in ether. The same compound is also formed by the oxidation of *dithiomethylbenzylidene*, CHPh($SMe)_2$. This is prepared by the action of gaseous hydrogen chloride on a mixture of benzaldehyde and methyl mercaptan, and forms a colourless, mobile liquid.

The disulphones of meta- and para-nitrobenzylidene prepared from the corresponding acids both crystallise in slender, yellowish needles, which melt at 178—179° and at 247—248° respectively.

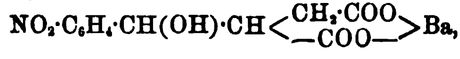
N. H. M.

Preparation and Nitration of Dibenzylmalonic Acid. By J. C. A. S. THOMAS (*Rec. Trav. Chim.*, **6**, 87—90).—Ethyl dibenzylmalonate obtained by the interaction of ethyl malonate, alcohol, sodium, and benzyl chloride, forms white crystals melting at 13—14°. 30 grams of this ethereal salt is dissolved in 20—30 c.c. of alcohol, and 20 grams of potash added gradually in coarse powder. Heat is developed, but on cooling the mass becomes almost solid. It is allowed to stand overnight, and is heated to drive off the alcohol. The product then separates into two layers, the upper consisting probably of half-saponified salt. Concentrated aqueous potash is added, and the mixture heated on a water-bath for several hours and then acidified with hydrochloric acid. Evolution of carbonic anhydride indicates the formation of some dibenzylacetic acid. Dibenzylmalonic and dibenzylacetic acids are separated by taking advantage of the fact that the former is somewhat soluble in water, but is insoluble in light petroleum; whilst the latter is almost insoluble in boiling water, but is somewhat soluble in light petroleum. Dibenzylmalonic acid crystallises in needles, which melt at 171°, as stated by Perkin (Trans., 1885, 821), and when added to cooled nitric acid of sp. gr. 1·52, precipitated with water, and the product purified by solution in acetic acid and precipitation with water, it yields a dinitro-derivative, $C_{17}H_{14}N_2O_8$; this forms a white crystalline powder, melting at 155°, with evolution of gas. This product is not homogeneous, for if the acetic acid solution is fractionally precipitated by adding water, the first fraction melts at 160°, and the last becomes soft at 95°, and is completely melted at 110°. C. H. B.

Nitrophenylparaconic Acids. By H. W. Salomonson (*Rec. Trav. Chim.*, 6, 1—22).—Phenylparaconic acid can be converted into α-naphthol with intermediate formation of phenylisocrotonic acid, and the author prepared the nitrophenylparaconic acid with a view to obtain nitronaphthol in a similar manner. Nitrophenylparaconic acid, however, does not yield nitrophenylisocrotonic acid, and hence does not yield nitronaphthol.

Metanitrobenzaldehyde, sodium succinate, and acetic anhydride, in molecular proportion, were heated together at 125° for four hours, the product treated with water, the solution extracted with ether, and the aqueous liquid acidified with hydrochloric acid. A precipitate is thus obtained which can readily be crystallised from warm water. The ethereal solution, which contains metanitrobenzoic acid and metanitrophenylparaconic acid, is neutralised with sodium carbonate, acidified with hydrochloric acid, and the precipitate subjected to fractional crystallisation. The metanitrobenzoic acid melts at 141°.

Metanitrophenylparaconic acid melts at 171°. Neither the acid nor its salts contain water of crystallisation, and in this respect it differs from phenylparaconic acid. The acid cannot be distilled in a vacuum, and carbonises at 230—250°, these properties being common to all its derivatives. It is carbonised when heated with water in sealed tubes at 200—220°, but is not decomposed by dilute sulphuric acid under the ordinary pressure, and is not affected by dilute sulphuric acid, glacial acetic acid, or acetic anhydride, in sealed tubes at 170°, although at a higher temperature it carbonises. It is dissolved by cold concentrated sulphuric acid, and is precipitated unchanged on addition of water, even if the solution has been heated to the point of carbonisation. Metanitrophenylparaconic acid is soluble in warm water, alcohol, glacial acetic acid, ethyl acetate, and glycerol, but not in carbon bisulphide or benzene.

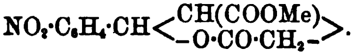
Since metanitrophenylparaconic acid is the lactone of nitrophenylitamalic acid, it forms two series of salts. *Barium metanitrophenylitamalate*,  $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH\left<\begin{array}{c}CH_2\cdot COO\\ —COO—\end{array}\right>Ba$, is obtained by dissolving the acid in ammonia, adding a solution of barium chloride, and boiling for a short time. The metanitrophenylparaconates are obtained by dissolving the acid in ammonia, heating to expel excess of ammonia, and adding soluble metallic salts. The silver salt forms colourless needles; the copper salt pale blue crystals; and the lead salt small needles.

Paranitrophenylparaconic acid is obtained from paranitrobenzaldehyde in a precisely similar manner. It crystallises from boiling water in small, white, nacreous leaflets; from acetic acid in cubes. It melts at 163°, and is soluble in warm water, ethyl acetate, alcohol, and sulphuric acid; is slightly soluble in ether, but does not dissolve in cold water, light petroleum, benzene, or carbon bisulphide. With barium hydroxide, it yields *barium paranitrophenylitamalate*, which forms small white crystals. *Silver paranitrophenylparaconate* crystallises in needles; the copper salt also crystallises from water.

Both the meta- and para-derivatives are strong acids, and liberate acetic acid from sodium acetate.

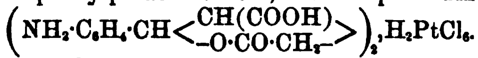
Barium paranitrophenylitamalate, when treated with hydrochloric acid in the cold, the solution extracted with ether, and the ethereal solution allowed to evaporate spontaneously, yields free paranitrophenylitamalic acid as a yellow amorphous residue. If a solution of nitrophenylparaconic acid in concentrated ammonia is heated with acetic acid, and then mixed with barium chloride, no precipitate is formed, hence it is evident that nitrophenylitamalic acid is converted by acetic acid into nitrophenylparaconic acid.

If a solution of meta- or para-nitrophenylparaconic acid in methyl alcohol is saturated with hydrogen chloride, and then mixed with water, it yields a resinous precipitate, which, after being dried for a week over potassium hydroxide and sulphuric acid, contains no chlorine, from which it follows that the lactone-group has remained intact. The resinous product is the methyl salt of the acid



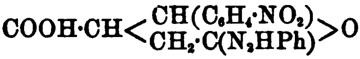
$$NO_2\cdot C_6H_4\cdot CH\left<\begin{matrix}CH(COOMe)\\ -O\cdot CO\cdot CH_2-\end{matrix}\right>.$$

Ethyl paranitrophenylparaconate is obtained by heating the acid and alcohol with strong sulphuric acid. Its properties are similar to those of the methyl salt. Both are soluble in benzene, ether, sulphuric acid, and chloroform.

Both acids are rapidly reduced by tin and hydrochloric acid at the ordinary temperature, but the products can only be isolated in the form of platinochlorides, which are easily soluble in water and alcohol, but are insoluble in benzene, ether, and chloroform. The product of reduction is amidophenylparaconic acid, and the platinum salt has the composition  $\left(NH_2\cdot C_6H_4\cdot CH\left<\begin{matrix}CH(COOH)\\ -O\cdot CO\cdot CH_2-\end{matrix}\right>\right)_2,H_2PtCl_6$. The hydrochloric acid solution of the amido-acid gives no precipitate with gold chloride, or sulphuric, hydrobromic, hydriodic, or acetic acids. If after reduction and separation of the tin the solution is rapidly concentrated until viscous, and placed in a vacuum over potash and sulphuric acid, the metamidophenylparaconic acid will sometimes crystallise, but the para-derivative always remains as a syrup. If the liquid is now heated to 60—70° to expel water and hydrogen chloride, the amido-acid is obtained in groups of prismatic crystals, insoluble in benzene, chloroform, and ether, but very hygroscopic, and easily soluble in water or ethyl alcohol. If heated rapidly it carbonises; with nitrous acid, no diazo-compound is obtained.

Hydriodic acid completely reduces both the nitro-acids when heated in sealed tubes at 130°, but not at 100°. This method, however, is inconvenient.

Metanitrophenylparaconic acid, heated at 130° with phenylhydrazine in molecular proportion, allowed to cool, and treated first with dilute acetic acid and then with warm water, yields a derivative,



$$COOH\cdot CH<\begin{matrix}CH(C_6H_4\cdot NO_2)\\ CH_2\cdot C(N_2HPh)\end{matrix}>O,$$

which melts at 130—132° with decomposition.

Orthonitrophenylparaconic acid was obtained in a similar manner, but the yield was small, and the acid was not isolated. C. H. B.

Formation of Monosulphones. By R. OTTO (*Ber.*, **21**, 652—658).—When methylene-iodophenylsulphone reacts with sodium benzenesulphinate in alkaline solution, in sealed tubes at about 200°, the products are methylphenylsulphone, ethyl ether, phenyl mercaptan, ethylphenyl sulphide, phenyl bisulphide, iodine, hydriodic acid, benzenesulphonic acid, and sodium iodide, benzenesulphonate, sulphate, and iodate. The primary reaction is evidently that in which the methylphenylsulphone is formed; most of the other products being due to secondary reactions. The reaction between methylene-iodoparatolylsulphone and sodium paratoluenesulphinate seems to be quite analogous, methylparatolylsulphone being formed.

Methylene-iodoparatolylsulphone is prepared by heating equimolecular proportions of sodium toluenesulphinate and methylene iodide dissolved in alcohol, in a reflux apparatus; it forms small needles, and melts at 136°.

When methylene-iodophenylsulphone is heated with sodium ethoxide and alcohol at 70—80°, it is readily converted into methylphenylsulphone; in this case, the eliminated oxygen is mainly used up in converting the iodide into iodate, although small quantities of other oxidation products are formed. In the case of the corresponding chloro-compound, benzenesulphinic acid is also formed.

By the action of sodium ethoxide on dichlormethylphenylsulphone in alcoholic solution, the latter is converted partly into the monochloro-derivative, partly into sodium benzenesulphonate with a trace of sulphinate.

From these and other experiments, some of which are not yet published, the author deduces the law:—Dihalogen-derivatives of hydrocarbons, fatty acids, and their ethereal salts, in which the halogen-atoms are united to the same carbon-atom, when treated with alkaline sulphinates only exchange a single halogen-atom for the group $R'SO_2$; the second halogen-atom, in the presence of water, being displaced by hydrogen. A. J. G.

Methylenechlorophenylsulphone. By R. OTTO (*Ber.*, **21**, 658—659).—*Methylenechlorophenylsulphone*, $CH_2Cl·SO_2Ph$, is best prepared by heating an aqueous solution of sodium dichloracetate and sodium benzenesulphinate in molecular proportions. It crystallises in plates, melts at 52°, and is readily soluble in hot alcohol, nearly insoluble in cold water. It is not formed by the action of chlorine on a solution of methylphenylsulphone in carbon tetrachloride. When reduced with sodium amalgam in alcoholic solution, it yields sodium benzenesulphinate and some gaseous product, probably ethane or ethylene. With zinc and sulphuric acid, it gives methylphenylsulphone.

Attempts to convert it into ethylenediphenylsulphone by the action of sodium or sodium-amalgam in benzene solution, were without result. A. J. G.

Identity of Diphenyldiisoindole and 3′ Phenylindole. By R. MÖHLAU (*Ber.*, **21**, 510—511).—A comparison of diphenyldiisoindole and 3′ phenylindole showed them to be identical, and a vapour-density determination made with the former compound pointed to the formula $C_{14}H_{11}N$, and not $C_{28}H_{22}N_2$ (Abstr., 1883, 342. Compare also Wolff, this vol., p. 371.) N. H. M.

Indolecarboxylic Acids. By G. CIAMICIAN and G. MAGNANINI (*Ber.*, **21**, 671—673).—Carboxylic acids cannot be prepared from methylketole and scatole by the ammonium carbonate reaction, but are readily obtained by heating with sodium in a stream of carbonic anhydride at 230—250°.

Methylketolecarboxylic acid crystallises in needles, and decomposes into methylketole and carbonic anhydride when heated alone at 183°, or when its ammoniacal solution is heated. The scatolecarboxylic acid is identical with that described by H. and E. Salkowski (Abstr., 1880, 413; 1885, 569).

When acetylmethylketole is oxidised with potassium permanganate, it yields acetylorthamidobenzoic acid; when, however, the oxidation is effected by fusion with potash, α-indolecarboxylic acid is formed. The same acid is obtained when methylketole is fused with potash, whilst scatole yields β-indolecarboxylic acid.

Acetylskatole is best prepared by the action of acetic chloride and some zinc chloride on skatole at the ordinary temperature; it forms long, slender needles, and melts at 147—148°. A. J. G.

Hydrogenation of Triphenylmethane. By M. GOLENKIN (*J. Russ. Chem. Soc.*, 1887, 166—171).—For the purpose of hydrogenation, 1 gram of triphenylmethane was sealed up in tubes with 15 c.c. of hydriodic acid and 0·5 gram of red phosphorus, and the mixture heated gradually to 280°, the tubes being opened and sealed up again several times in order to remove the gases formed in large quantities. When the reaction was over, the tubes were found to contain a small quantity of liquid hydrocarbon (3·5 grams from 12 grams of triphenylmethane) consisting of a mixture of benzene and toluene, but no hydrogenation of the triphenylmethane took place. B. B.

Derivatives of Orthotolidine. By A. Gerber (*Ber.*, **21**, 746—750).—*Diacetylorthotolidine*, $C_{14}H_{12}(NHAc)_2$, obtained by heating tolidine with glacial acetic acid in a reflux apparatus, forms lustrous, white needles, melts at 314°, sublimes at a still higher temperature with partial decomposition, and only dissolves readily in phenol.

Tetracetylorthotolidine, $C_{14}H_{12}(NAc_2)_2$, is prepared by heating the diacetyl compound with acetic anhydride at 160—170° for about six hours; it forms snow-white, lustrous needles, melts at 211°, and is very readily soluble in the ordinary solvents. When heated with concentrated hydrochloric acid, it is reconverted into the diacetyl compound.

Dinitrodiacetylorthotolidide, $C_{14}H_{12}(NHAc)_2(NO_2)_2$, forms nearly white crystals, decomposes without previous fusion at 320°. When saponified, it yields *dinitro-orthotolidine* $[Me_2 : (NH_2)_2 : (NO_2)_2 = 3 : 3' : 4 : 4' : 5 : 5']$; this forms shimmering, garnet-red needles, melts at 266—267°, explodes at a few degrees higher, and when reduced with zinc-dust, is converted into a ditoluylenediamine which yields an azine with phenanthraquinone, and therefore must have the amido-groups in the ortho-position.

Orthodicresol, $C_{14}H_{12}(OH)_2$, is prepared by diazotising orthotolidine and boiling the product with dilute sulphuric acid. It forms a white, crystalline powder, melts at 160—161°, and is sparingly soluble in boiling water, readily in alcohol, ether, acetic acid, and in boiling benzene hydrocarbons. A *dinitro*-derivative is prepared by boiling the diazotised product with nitric acid; it crystallises in golden-yellow needles, melts at 272—273°, sublimes with partial decomposition, is insoluble in water, alcohol, and ether, and dissolves in hot alkalis to form salts which crystallise in stellate groups; the potassium and sodium salts are reddish-violet, the ammonium salt orange-red.

A. J. G.

Thio-derivatives of Desoxybenzoïn and its Analogues. By V. Meyer (*Ber.*, **21**, 353—355).—The compound obtained by Bergreen by the action of thiocarbonyl chloride on sodium ethoxide and desoxybenzoïn (this vol., p. 446) possesses much interest, since, in addition to its remarkable properties, it affords the first instance of the displacement of both hydrogen-atoms of the methylene group in desoxybenzoïn by a radicle containing carbon (compare this vol., p. 147). The compound has a fiery, golden-yellow colour, and in appearance resembles the most beautiful yellow organic dyes. Concentrated sulphuric acid dissolves it, forming a deep violet-coloured solution from which water precipitates the compound unchanged. When heated with pyrosulphuric acid, it is converted into a yellow sulphonic acid, which yields a sparingly soluble barium salt and readily soluble alkaline salts. The substance itself, however, is too sparingly soluble to admit of its employment as a dye, whilst the sulphonic acid is almost destitute of tinctorial properties. It is improbable that the compound has the composition expressed by the formula $CO\cdot Ph\cdot CPh\colon CS$, since this would in no way correspond with its properties, which differ in so marked a manner from those of the thio-derivatives of ethyl malonate and ethyl acetoacetate prepared under like conditions by Bergreen (*loc. cit.*); on the contrary, the author regards it as a polymeride, and proposes to determine its molecular weight by Raoult's method: in the meantime, it is suggested that it is either a derivative of a six-carbon "ring" or a thiophen-derivative formed by a condensation analogous to that occurring in the formation of thiazoles (this vol., p. 256).

The ketones, $CH_2Ph·CO·C_6H_4Me$ and $CH_2Ph·CO·C_4SH_3$, form corresponding compounds when treated with thiocarbonyl chloride and, under like conditions, the phenylated desoxybenzoïn,

$$CH_2Ph·CO·C_6H_4Ph,$$

also yields a yellow compound which, however, dissolves in sulphuric acid with a green colour. These compounds are extremely stable; the thiophen-derivative for example, when heated with fuming nitric acid is converted into a yellow nitro-derivative, which gives no colour reaction with sulphuric acid.

Methyldesoxybenzoïn, COPh·CHMePh, and its homologues do not react with thiocarbonyl chloride, and hence this reagent affords a ready means of discriminating between primary and secondary derivatives of desoxybenzoïn.

Thiocarbonyl chloride cannot be employed to distinguish between primary and secondary benzyl cyanides. Benzyl cyanide, however, reacts with a mixture of sodium ethoxide (1·4 parts of sodium in 20 parts of alcohol) and benzaldehyde forming the nitrile of phenylcinnamic acid, CHPh:CPh·CN, which melts at 88°, whilst the nitrile of hydratropic acid, CHMePh·CN, does not form a condensation compound under similar conditions. This method can not only be used qualitatively, but may also be employed to separate benzyl cyanide from a mixture of the two compounds. W. P. W.

Oximes of Benzil. By N. POLONOWSKA (*Ber.*, **21**, 488—491).—When benzilmonoxime in alcoholic solution is reduced with $2\frac{1}{2}$ per cent. sodium amalgam in presence of acetic acid, diphenylhydroxyethylamine is obtained. No tetraphenylaldine is formed, as when the reduction is effected by means of tin and hydrochloric acid (Braun and Meyer, this vol., p. 367). When benzildioxime is reduced with sodium amalgam, tetraphenylaldine (*loc. cit.*) is obtained; ammonia is formed in the reaction. The yield of tetraphenylaldine is small.

N. H. M.

Intramolecular Change in Benzildioxime. By E. GÜNTHER (*Ber.*, **21**, 516—518).—When benzildioxime is heated with a solution of hydrogen chloride in glacial acetic acid and acetic anhydride, a diacetyl-compound is formed which, when saponified, yields Goldschmidt's isobenzildioxime, melting at 206° (Abstr., 1884, 62).

The compound (m. p. 121—122°) obtained by the action of phosphorus pentachloride on benzildioxime (Beckmann, Abstr., 1887, 826) is a dichloride, NCl:CPh·CPh:NCl; two other nitrogenous compounds melting at 146° and 95° respectively, are also formed in the reaction. The chloride could not be obtained from isobenzildioxime.

N. H. M.

Hydrodiphthallactonic Acid and Hydrodiphthalyl. By E. HASSELBACH (*Annalen*, **243**, 249—272).—Wislicenus (Abstr., 1885,

57) has shown that diphthalyl, hydrodiphthalyl, and hydrodiphthallactonic acid are formed by the action of acetic acid and zinc-dust on phthalic anhydride, also that hydrodiphthallactonic acid,

$$CO{<}\begin{smallmatrix}C_6H_4\\ -O-\end{smallmatrix}{>}CH\cdot CH_2\cdot C_6H_4\cdot COOH,$$

is converted into hydroxydiphthalylic acid,

$$COOH\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot COOH,$$

by boiling with potash.

Silver hydroxydiphthalylate decomposes at 225° in a vacuum, yielding water, phthalic anhydride, and other products. The *ethyl* salt is a thick liquid which slowly crystallises. Hydrodiphthallactonic acid is converted into *stilbenediorthocarboxylic acid*,

$$COOH\cdot C_6H_4\cdot CH : CH\cdot C_6H_4\cdot COOH,$$

by the action of potassium cyanide at 215°. This acid when reduced with hydriodic acid forms dibenzyldiorthocarboxylic acid. Stilbene diorthocarboxylic acid begins to melt at 250°, and is converted at this temperature into hydrodiphthallactonic acid. The ethyl salt forms small needles and melts at 79—80°.

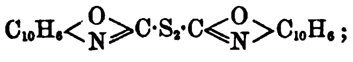
Hydrodiphthallyl (m. p. 250°) dissolves in alkalis, yielding salts of dihydroxybenzyldiorthocarboxylic acid, $C_{16}H_{14}O_6$. The free acid has not been isolated; on the addition of acetic acid to its salts, an acid is deposited having the composition $C_{16}H_{12}O_5$; this acid is converted into hydrodiphthallyl at 190° or by heating with acetic anhydride. The precipitate which is formed when hydrochloric acid is added to a solution of hydrodiphthallyl in alkalis is not a definite chemical compound, but a mixture consisting chiefly of hydrodiphthalyl. Hydrodiphthallactonic acid is not the sole product of the reduction of diphthalyl with zinc and potassium hydroxide; hydrodiphthalyl is always formed in small quantities. Hydrodiphthalyl is partly converted into hydrodiphthallactonic acid by reduction with zinc-dust in alkaline solutions. W. C. W.

Derivatives of α-Naphthol. By O. N. Witt (*Ber.*, **21**, 321—325).—In addition to α-naphtholsulphonic acid, *α-hydroxynaphthyl methyl ketone*, $OH\cdot C_{10}H_6\cdot COMe$, is obtained on sulphonating α-naphthol in acetic acid solution, and is also formed by heating equal weights of α-naphthol and acetic acid with zinc chloride as in Nencki and Sieber's method of preparing analogous compounds (Abstr., 1881, 591, 811). It crystallises from benzene in six-sided prisms, from alcohol in needles, melts at 103°, has a pale-green colour, and is insoluble in water. Sulphuric acid dissolves it with a red, alkalis with a pure yellow colour. The alkaline salts crystallise in long, citron-yellow needles, and are decomposed by carbonic anhydride. In alkaline solution, it yields an intense reddish-brown colour with orthonitrobenzaldehyde, but does not form an indophenol on treatment with paradiamines either in the presence of air or of oxidising agents. A comparison of the azo-colours obtained from the ketone with the corresponding α-naphthol-derivatives shows that the shade of colour is invariably more yellow in the case of the former. The *oxime* crystallises from dilute alcohol in long, pale-yellow needles, and melts at 168—170° with decomposition. When heated with 12 per cent. alcoholic ammonia at 180—200°, the ketone is converted into the *ketimide*, $OH{\cdot}C_{10}H_6{\cdot}CMe{:}NH$, which crystallises from alcohol in long, golden-yellow needles, melts at 203° with decomposition, and is decomposed into its constituents on treatment with acids or alkalis.

β-Naphthol, when heated with acetic acid and zinc chloride, does not form a compound corresponding with α-hydroxynaphthyl methyl ketone. W. P. W.

Action of Carbon Bisulphide on Benzene-azo-β-Naphthol. By P. JACOBSON (*Ber.*, **21**, 414—422).—By the action of carbon bisulphide on benzene-azo-β-naphthol, phenyl thiocarbimide, sulphur, thiocarbamidonaphthol, and carbanilamidonaphthol are formed. This reaction shows that under certain conditions benzene-azo-β-naphthol is capable of reacting as though it were a true azo-compound, for its explanation is difficult on the hydrazide formulæ proposed by Liebermann (Abstr., 1884, 610) and by Zincke and Lawson (*Ber.*, **20**, 2903), although at the same time the insolubility in alkalis precludes the substance being regarded as an azo-compound.

Thiocarbamidonaphthol, $C_{10}H_6{<}\genfrac{}{}{0pt}{}{O}{N}{>}C{\cdot}SH$, is obtained, together with the products mentioned above, by heating benzene-azo-β-naphthol with five times its weight of carbon bisulphide for 8 to 12 hours at 250°; it is separated from the other products by means of its insolubility in carbon bisulphide and its solubility in alkalis. It crystallises in long, colourless needles, melts at 248—249°, and is sparingly soluble in benzene, readily soluble in hot acetic acid, and very readily soluble in cold alcohol. When heated for some hours at 150—180° with hydrochloric acid, it yields amido-β-naphthol. From the latter, it can be re-formed by heating with carbon bisulphide. When boiled with aniline, hydrogen sulphide is evolved and carbanilamidonaphthol formed. By the action of an alcoholic solution of iodine, it is converted into the corresponding *bisulphide*,



$$C_{10}H_6{<}\genfrac{}{}{0pt}{}{O}{N}{>}C{\cdot}S_2{\cdot}C{<}\genfrac{}{}{0pt}{}{O}{N}{>}C_{10}H_6;$$

this crystallises in tufts of microscopic needles, is readily soluble in hot benzene and acetic acid, nearly insoluble in hot alcohol.

Carbanilamidonaphthol, $C_{10}H_6{<}\genfrac{}{}{0pt}{}{O}{N}{>}C{\cdot}NHPh$, the main product of the reaction, forms small colourless needles, melts at 167—168°, and is very readily soluble in cold alcohol, sparingly soluble in boiling hydrochloric acid, and insoluble in alkalis. The *acetate* crystallises in lustrous, flat needles and melts at 120—130°. The *picrate* melts at 209—210°. When heated with hydrochloric acid for four hours at 180—190°, it is resolved into amidonaphthol, carbonic anhydride, and aniline. A. J. G.

Substitution of the Acetyl-group for the Amido-group by Aid of the Diazo-reaction. By R. MELDOLA (*Ber.*, **21**, 601).—The compounds formed by the action of nitrous acid on meta- and para-nitrobenzene-azo-β-naphthylamine are readily decomposed by glacial acetic acid with formation of the acetyl-derivatives of the corresponding β-naphthol-compounds. For instance, if nitrobenzene-azo-β-naphthylamine is dissolved in hot (not boiling) acetic acid and the necessary amount of sodium nitrite added, *metanitrobenzene-azoacetyl-β-naphthol* soon separates; it crystallises in hair-like, red needles, and melts at 161—162°; when heated for ½ hour with alcoholic potash, metanitrobenzene-azo-β-naphthol is readily obtained.

This method gives a means of displacing the amido-group by the acetyl-group, and will probably be of general applicability for the synthesis of phenol-derivatives containing different acid radicles.

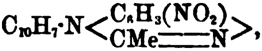
A. J. G.

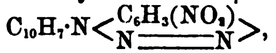
Nitro-derivatives of Phenyl-β-Naphthylamine. By E. HEIM (*Ber.*, **21**, 589—594).—*Dinitrophenyl-β-naphthylamine*,

$$C_{10}H_7{\cdot}NH{\cdot}C_6H_3(NO_2)_2\ [NH : (NO)_2 = 1 : 2 : 4],$$

is formed by the action of bromodinitrobenzene (m. p. 72°) on an alcoholic soltuion of β-naphthylamine. It crystallises in crimson prisms, melts at 169·5°, is soluble in acetic acid, acetone, hot benzene, and ether, very sparingly soluble in alcohol, and insoluble in water. The reduction-products obtained by the action of iron and acetic acid, and of stannous chloride and hydrochloric acid, could not be isolated.

Nitramidophenyl-β-naphthylamine, $[NH : NH_2 : NO_2 = 1 : 2 : 4]$, is prepared by reducing the dinitro-compound with ammonium sulphide; it is dimorphous, crystallising in brown needles of cantharidine lustre, or in small, crimson prisms, it melts at 195°; and is very readily soluble in ether, acetic acid, acetone, and chloroform, moderately soluble in alcohol, benzene, and its homologues, insoluble in light petroleum. The *acetyl*-derivative forms lustrous, orange-red needles, which melt below 200° with decomposition.

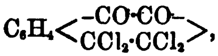
Nitrophenylethenylamido-β-naphthylamine,  $C_{10}H_7{\cdot}N{<}\begin{matrix}C_6H_3(NO_2)\\ CMe{=\!=}N\end{matrix}{>}$, is prepared by heating nitramidophenyl-β-naphthylamine with ten times its weight of acetic anhydride for seven hours in a reflux apparatus; it forms pale-yellow, lustrous needles, melts at 162°, is readily soluble in alcohol and ether, still more so in benzene, toluene, acetone, and chloroform, and dissolves in acids. The formation of this anhydro-base leaves no doubt that in nitramidophenyl-β-naphthylamine, the amido- and imido-groups are relatively in the ortho-position.

Nitrazoimidophenyl-β-naphthylamine,  $C_{10}H_7{\cdot}N{<}\begin{matrix}C_6H_3(NO_2)\\ N{=\!=}N\end{matrix}{>}$, is obtained by the action of nitrous acid on the nitramido-compound; it crystallises in delicate, white needles, melts at 203—204°, is sparingly soluble in alcohol, readily in ether, acetic acid, benzene, chloroform, and acetone, and is indifferent to reagents. A. J. G.

Ketonaphthol (Aceto-α-Naphthol). By H. ERDMANN (*Ber.*, **21**, 635—636).—*Ketonaphthol*, $C_{10}H_6Ac{\cdot}OH$ $[OH : Ac = 1 : 3]$, was obtained by the author in 1886, by the distillation of benzallevulinic acid; it melts at 167°, is rather sparingly soluble in benzene in the cold, dissolves in concentrated sulphuric acid with orange-yellow colour, gives intensely yellow compounds with alkalis, unites with diazo-compounds to form colouring matters identical in tint with the corresponding compounds from α-naphthol, and gives indophenol reactions with quinonechlorimides. Witt's α-hydroxynaphthyl methyl ketone (this vol., p. 486) is evidently closely related in properties.

A. J. G.

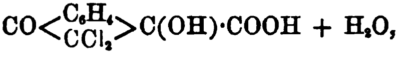
β-Naphthaquinone. By T. Zincke (*Ber.*, **21**, 491—501; compare this vol., p. 158).—*Tetrachlorodiketohydronaphthalene*,



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{-CO\cdot CO-}\\ \mathrm{CCl_2\cdot CCl_2}\end{matrix}>,$$

is prepared by passing chlorine into a solution of orthamidonaphthol hydrochloride in 15 parts of glacial acetic acid until the liquid is yellow; the product is kept for two days in a closed vessel, precipitated with water, and crystallised from dilute acetic acid. The anhydrous compound is obtained by heating the substance at 100—105°, and crystallising it from anhydrous ether free from alcohol, some light petroleum being added. It forms large, transparent, lustrous, monoclinic crystals of a pale-sulphur colour, readily soluble in ether, carbon bisulphide, and glacial acetic acid, less soluble in light petroleum; it melts at 90—91°, and decomposes at 180° into dichloro-β-naphthaquinone and chlorine. When the acetic acid solution is heated with potassium iodide, dichloro-β-naphthaquinone is formed. It is converted by stannous chloride and by sulphites into dichloro-β-naphthaquinol. Tetrachlorodiketohydronaphthalene, precipitated by water, forms small, lustrous plates with 3 mols. H_2O, and melts at 86°. It can also be obtained in lustrous needles (with 1 mol. H_2O) which melt at 87°. When the crystals with 3 mols. H_2O are recrystallised from ether, large, monoclinic crystals, melting at 90—91° are obtained, and resemble the anhydrous crystals, except that they are white. When the tetrachloro-compound is crystallised from alcohol, a *monethylate* separates in white crystals, melting with effervescence at 103°.

Dichlorodiketohydroxyhydrindocarboxylic acid,



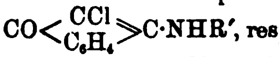
$$\mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CCl_2}\end{matrix}>\mathrm{C(OH)\cdot COOH + H_2O},$$

obtained by dissolving the diketohydrate in dilute sodium carbonate solution, forms large, colourless, monoclinic crystals, melting at 138—139°, readily soluble in alcohol, benzene, and glacial acetic acid, When boiled with baryta-water, it decomposes, probably with formation of the compound $\mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CCl}\end{matrix}\geqslant\mathrm{C\cdot OH}$. The *methyl salt* forms large, lustrous, monoclinic crystals, melting at 123—124°. The *acetyl-compound*, $\mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CCl_2}\end{matrix}>\mathrm{C(OAc)\cdot COOH}$, crystallises in small prisms melting at 126°.

Dichloro-α-diketohydrindonaphthene, $\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}>\mathrm{CCl_2}$, prepared by oxidising the hydroxy-acid with chromic acid, crystallises from dilute alcohol in small, lustrous plates, melting at 124—125°.

Trichlorovinylbenzoylcarboxylic acid, $CCl_2{:}CCl{\cdot}C_6H_4{\cdot}CO{\cdot}COOH$, is formed in small quantity when the tetrachlorodiketone is dissolved in sodium carbonate. It was obtained as an oil, and was not purified.

When the tetrachlorodiketone is dissolved in soda, and the solution acidified with acetic acid and warmed with chromic acid, trichlorovinylbenzoic acid (Abstr., 1887, 955) is obtained.

The diketone, $C_8H_4O_2Cl_2$, described above, is identical with the compound previously obtained by the action of phosphoric chloride on the hydroxy-derivative from the dichloroketone, $C_8H_4OCl_2$ (Abstr., 1887, 728). The hydroxy-derivative, and the amine by means of which it is obtained, must, therefore, have the constitution represented by the formulæ $CO<{CCl \atop C_6H_4}>C{\cdot}OH$ and  $CO<{CCl \atop C_6H_4}>C{\cdot}NHR'$, respectively.

N. H. M.

Action of Bromine on the Naphthaquinoneoximes. By C. Brömme (*Ber.*, **21**, 386—391).—When a slight excess of bromine is added to a solution of naphtha-β-quinone-α-oxime in chloroform, an additive compound, $C_{10}H_7NO_2Br_2$, is formed, which crystallises in colourless needles, melts at 130—131°, and is not very stable. When heated in solution in acetic acid or in alcohol, or when dissolved in alkalis, it loses hydrogen bromide and is converted into *β-bromonaphtha-β-quinone-α-oxime*, $C_{10}H_5BrO{:}NOH$ [NOH : O : Br = 1 : 2 : 3]; this forms long, yellow needles, melts at 172°, is soluble in alcohol, ether, benzene, chloroform, light petroleum, and acetic acid with brown colour, in concentrated sulphuric acid with purple, and in alkalis with brownish-green colour. It is also formed if the bromination is conducted in acetic acid solution in the cold; if, however, it is effected in hot solution, a *bromonaphthaquinone* is formed which melts at 200—201°, is soluble in alcohol, ether, &c., and is also formed by heating β-naphthaquinoneoxime dibromide or bromo-β-naphthaquinoneoxime with concentrated hydrochloric or acetic acids. When this is treated with aqueous sulphurous acid, it is converted into *bromonaphthaquinol*; this crystallises in yellow needles, melts at 193°, and is reconverted into the quinone by oxidation with chromic acid. The quinone, when treated with soda or alcoholic ammonia, gives the known bromhydroxynaphthaquinone (m. p. 196·5°), and with aniline yields β-bromo-β-anilido-α-naphthaquinone, thus entirely differing from Zincke's β-bromo-β-naphthaquinone.

Naphtha-α-quinone-β-oxime dibromide, obtained by the action of bromine on naphtha-α-quinone-β-oxime, forms grey plates, melts at 154—155°, and is more stable than its isomeride. The corresponding *β-bromonaphtha-α-quinone-β-oxime*, [O : NOH : Br = 1 : 2 : 3], separates from alcohol in yellow, from acetic acid in dark-brown crystals, melts at 175°, and is soluble in alcohol, chloroform, acetic acid, benzene, ether, light petroleum and sulphuric acid, with brown colour, and in alkalis with orange colour.

β-Dibrom-α-naphthaquinoneoxime is obtained by the bromination of naphtha-α-quinone-α-oxime in either hot or cold acetic acid, an additive

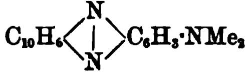
compound seeming not to be formed; it crystallises in white needles, melts at 174—175°, and is soluble in the usual solvents except light petroleum and carbon bisulphide. A. J. G.

Action of Monamines on the Naphthaquinoneoximes. By C. BRÖMME (*Ber.*, **21**, 391—395).—Anilidonaphthaquinonanilide is formed when either of the three naphthaquinoneoximes is treated with aniline and glacial acetic acid. The mother-liquor contains a violet, crystalline substance, which melts at 260°. *Dinitroanilidonaphthaquinonanilide*, $C_{22}H_{14}N_2O(NO_2)_2$, is a reddish-brown, crystalline substance, which melts at 143° and is sparingly soluble in alcohol.

Paratoluidonaphthaquinoneparatoluidide, $C_{24}H_{20}N_2O$, forms long, red needles, and melts at 183°. The ψ-cumidine-derivative melts at 181°. The α-naphthylamine-derivative melts at 178°.

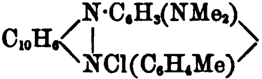
Anilidonaphthaquinonanilide, when heated with alcoholic hydrogen bromide or ethyl bromide, is converted into aniline and anilidonaphthaquinone. A. J. G.

β-Naphthylamine-δ-sulphonic Acid and β-Naphthylaminesulphonic Acid F. By H. ERDMANN (*Ber.*, **21**, 637—639).—The author confirms the identity of these acids. The diazo-compounds prepared from them show complete identity in every particular, and when heated with phosphoric chloride, both acids yield Cleve's δ-dichloronaphthalene. A. J. G.

Eurhodines and Saffranines. By O. N. WITT (*Ber.*, **21**, 719—725).—*Dimethylnaphtheurhodine*,  $C_{10}H_6{<}\overset{N}{\underset{N}{|}}{>}C_6H_3{\cdot}NMe_2$ [$N_2 = 1, 2$; $N : NMe_2 = 1, 2 : 4$], is prepared by heating 20 grams of nitrosodimethylaniline hydrochloride (3 mols.), 10 grams of β-naphthylamine (2 mols.), and 50 c.c. of glacial acetic acid in a capacious flask; the reaction commences below 100°, and the yield is the better the more slowly it is conducted. When the reaction is complete, the thin melt is poured into boiling water acidified with hydrochloric acid, and precipitated with sodium acetate; the brownish-red mass is dissolved in alcohol acidified with hydrochloric acid, the solution evaporated to a small bulk and mixed with concentrated hydrochloric acid, when the hydrochloride separates in copper-brown needles. From this, the free base is obtained by treatment with aqueous ammonia; it forms large, well-formed, rhombic tables, red by transmitted, and red or green, according to the faces, by reflected flight; it melts at 205°, sublimes in woolly flocks, dissolves in alcohol, ether, and the benzene hydrocarbons to yellow solutions with splendid yellow fluorescence. The solution in concentrated sulphuric acid is violet-red, and on dilution with water becomes successively black, green, grey, and bluish-violet. The salts are readily crystalline, have a bronzy lustre, and are dissociated by water. Dimethylparaphenylenediamine seems to be formed as a bye-product in the preparation.

Phenylnaphthylamine, when treated in like manner, yields a new dye which crystallises in black needles of metallic lustre, is soluble in water, is not precipitated by moderate addition of alkalis, and forms a sparingly soluble nitrate. The aqueous solution is decolorised by zinc-dust, but reoxidises on exposure to air. Satisfactory numbers could not be obtained on analysis.

When paratolyl-β-naphthylamine is treated in the manner described above, it is converted into a saffranine to which the constitution



$$C_{10}H_6\left<\begin{matrix}N\cdot C_6H_3(NMe_2)\\ |\\ NCl(C_6H_4Me)\end{matrix}\right>$$

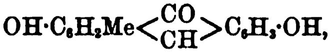
$[N_2 = 1, 2;\ N : Me = 1 : 4;\ N_2 : NMe_2 = 1, 2 : 4]$ is assigned. This crystallises in long, very slender needles of violet-metallic lustre, and like all saffranines is very hygroscopic and difficult to burn. It dissolves in water with bluish-violet colour, and dyes fibres violet; soda precipitates the free base in red flocks, soluble in alcohol with red colour and splendid orange-red fluorescence. The nitrate is so insoluble that the most dilute solution of the dye seems to be completely precipitated by addition of a drop of nitric acid. The platinochloride is at first obtained as an insoluble, gelatinous precipitate, which, on short digestion on the water-bath, changes into a heavy, crystalline powder, consisting of black, lustrous needles. A nitro-derivative was obtained in red crystals.

In this experimental evidence of the close relationship of an eurhodine and a saffranine-dye, the author sees a new proof of the correctness of the constitutional formulæ assigned by him to the saffranines.

A. J. G.

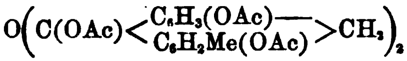
Naphthalene-derivatives. By O. N. Witt (*Ber.*, **21**, 726—728). —*Diparatolyldinaphthylamine*, $C_{20}H_{12}(NH\cdot C_6H_4Me)_2$, is obtained by heating 10 grams of paratolylnaphthylamine, 4 grams of nitrosodimethylaniline hydrochloride, 10 grams of zinc chloride, and 100 c.c. of glacial acetic acid on the water-bath. It forms lustrous, white crystals, melts at 224—225°, distils at higher temperatures with partial decomposition, and is dissolved by nearly all solvents. It does not give a picric acid compound, but gives a grass-green coloration with nitrous sulphuric acid. The nitroso-compound must be regarded as playing no part in the reaction beyond that of an oxidising agent, and may be replaced, although with diminished yield, by ferric chloride. An acetyl-compound was obtained, melting at 225°. When heated with hydrochloric acid at 220°, it is converted into paratoluidine and a resinous substance which can be obtained crystallised in needles melting at 193°. A. J. G.

Leuco-compounds from the Anthraquinone-dyes. By C. Liebermann (*Ber.*, **21**, 435—446).—*Chrysophanhydranthron*,



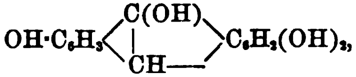
$$OH\cdot C_6H_2Me\left<\begin{matrix}CO\\ CH\end{matrix}\right>C_6H_3\cdot OH,$$

is prepared by heating to boiling chrysophanic acid with 15 times its weight of glacial acetic acid and three times its weight of tin, and then adding fuming hydrochloric acid in small portions, until the original deep yellow colour has changed to pale yellow, and the whole of the chrysophanic acid has dissolved. The product is filtered whilst boiling, precipitated with water, and recrystallised from benzene. It is also formed by reducing chrysophanic acid with zinc-dust and ammonia. It forms pale-yellow, microscopic plates, melts at 200—206°, and dissolves with difficulty in alkalis, the solution having a yellow colour and green fluorescence. The solution absorbs oxygen from the air, chrysophanic acid being reformed. It yields a peculiar acetyl-derivative, for which the constitution



$$O\left(C(OAc)<\begin{matrix}C_6H_3(OAc)-\!\!-\\C_6H_2Me(OAc)\end{matrix}>CH_2\right)_2$$

is suggested; this forms microscopic, yellowish-white plates, melts at 230—231°, and is readily soluble in acetic acid, sparingly in alcohol, and so closely resembles acetylchrysarobin that it was at first mistaken for it; the substances are, however, distinguished by their behaviour on hydrolysis with sulphuric acid, each yielding its parent substance.



Flavopurpuranthranol, $OH\cdot C_6H_3<\begin{matrix}C(OH)\\|\\CH-\!\!-\end{matrix}>C_6H_2(OH)_2$, obtained by the reduction of flavopurpurin in the manner described above, forms clear yellow needles readily soluble in alcohol, acetone, and acetic acid, sparingly in benzene, soluble in alkalis with yellowish-brown colour and greenish fluorescence. By acetylisation, a tetracetyl-compound is formed. On account of the instability of the anthranol, an attempt was made to combine the reduction with acetylisation. This method has proved of great use, where, from their instability, the leuco-compounds are very difficult to prepare. Flavopurpurin (1 part), sodium acetate (2 parts), zinc-dust (3 parts), and acetic anhydride (10 to 15 parts), are boiled together for a few minutes, cooled, thrown into much water, and left for some hours; the precipitate is then extracted with boiling acetic acid, when two products are obtained; a pentacetyl-derivative, $OAc\cdot C_6H_3{:}C_2(OAc)_2{:}C_6H_2(OAc)_2$, which crystallises in nearly colourless, yellow plates, and melts at 239—240°, and the tetracetyl-compound already mentioned, which forms nearly colourless flocks, and melts at 107—105°.

Anthrapurpuranthranol, $C_{14}H_6(OH)_4$, prepared by the reduction of anthrapurpurin, forms leather-yellow, microscopic needles, and yields a tetracetyl-derivative crystallising in needles and melting at 167°.

Anthragalanthranol, $C_{14}H_{10}O_4$, from anthragallol, crystallises in yellowish needles, does not show a definite melting point, and yields a triacetyl-derivative which melts at 203—205°. When an alkaline solution is exposed to the air, it assumes a beautiful violet colour, and on acidifying violet flocks separate, consisting of *anthragalhydroxyanthranol*, $C_6H_4{:}C_2(OH)_2{:}C_6H_2(OH)_2$.

Anthraflavanthranol, $C_{14}H_{10}O_3$, obtained by the reduction of anthraflavic acid, forms small, white needles. Its triacetyl-derivative crystallises in white needles, and melts at 165°.

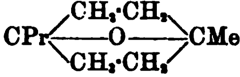
Rufigalanthranol was only obtained as its heptacetyl-derivative, $C_{14}H_3(OAc)_7$; this crystallises in pale-yellow needles. All these acetyl-derivatives show a characteristic fluorescence in alcoholic solution.

It is thus seen that the anthraquinone-dyes yield leuco-compounds on reduction. Although the evidence is not yet quite conclusive, it would seem that anthragallol, flavopurpurin, anthrapurpurin, and anthraflavic acid yield anthranols, whilst chrysophanic acid, alizarin, and isoanthraflavic acid yield the isomeric hydroanthranons.

When indigo is simultaneously reduced and acetylised, acetyl-indigo-white, $C_{16}H_{10}N_2O_2Ac_2$, is obtained in nearly white needles, which melt at 226°, and are pretty stable. A. J. G.

Terpenes and their Derivatives. By J. W. Brühl (*Ber.*, **21**, 457—477).—A continuation of the author's former paper on this subject (this vol., p. 377), in which the oxygen-derivatives of the terpenes are discussed. The physical properties of these are arranged in a table similar to that given in the case of the terpenes.

Menthol, $C_{10}H_{20}O$, is probably a derivative of menthene, with which it occurs in peppermint oil. It is lævorotatory, and its molecular refraction shows that it contains no double bond, and that its oxygen is united by single affinities. It is a secondary alcohol, and on oxidation yields the dextrorotatory menthone, $C_{10}H_{18}O$, a ketone the relation of which to menthol is similar to that of camphor, $C_{10}H_{16}O$, to borneol, $C_{10}H_{18}O$. By the action of hydrogen chloride, menthol is converted into the compound $C_{10}H_{19}Cl$. This, by loss of HCl, yields hydromenthene, $C_{10}H_{18}$, from the tetrabromide of which, by the removal of 4 mol. HBr, paracymene is obtained. Menthol is probably hydroxyhexahydroparacymene, [Pr : OH = 1 : 3].

Cineole, $C_{10}H_{18}O$, contains neither hydroxyl nor carbonyl, and yields, by loss of water, dipentene and also paracymene. It can form very unstable additive compounds, but according to its molecular refraction is a saturated compound. It is optically inactive, and optically inactive dipentene dihydrochloride is formed when hydrogen chloride is passed into warm cineole. Of the nine possible formulæ for cineole as a paracymene-derivative, only one,  $\mathrm{CPr}\left\langle\begin{array}{c}\mathrm{CH_2{\cdot}CH_2}\\ \text{——O——}\\ \mathrm{CH_2{\cdot}CH_2}\end{array}\right\rangle\mathrm{CMe}$, is in keeping with these facts.

Terpin, $C_{10}H_{20}O_2$, is an optically inactive compound formed by the action of alcoholic nitric acid on pinene. It is a saturated compound containing two hydroxyl-groups. By the action of hydrogen chloride on terpin, a compound, $C_{10}H_{18}Cl_2$, is formed, identical with the additive-product from dipentene and hydrogen chloride. Boiled with dilute mineral acids, terpin is first converted into terpineol, $C_{10}H_{18}O$, and then into dipentene. Terpineol contains one hydroxyl-group, has one double bond, and is optically active. In all probability terpin is a dihydroxy-, terpineol a monohydroxy-derivative of dipentene.

Camphor, $C_{10}H_{16}O$, probably also a derivative of the terpenes and paracymene, as it is easily obtained from camphene. From the molecular refraction of ethylcamphor, it is concluded that camphor contains no double bond. Borneol, the secondary alcohol derived from camphor, is also a saturated compound. From bornyl chloride, $C_{10}H_{17}Cl$, by elimination of HCl, camphene is obtained, so that borneol like camphor appears to be related to that terpene.

Isomeric with camphor are myristicol and absinthole. The first of these is an alcohol, and contains two double bonds. By the action of phosphorus chloride a compound $C_{10}H_{15}Cl$ is obtained, which on elimination of HCl yields paracymene. Myristicol is, therefore, probably a phenol of hydrated paracymene. Of absinthole but little is known; it is neither an aldehyde nor a ketone, but the oxygen is probably combined as in cineole.

Carvole and carvacrol, $C_{10}H_{14}O$. The molecular refraction is found to support Goldschmidt's views of the relation these substances bear to one another (Abstr., 1887, 475).

Safrole, $C_{10}H_{10}O$, contains according to the molecular refraction four double bonds, and from what is known of its chemical behaviour has most probably the constitution $C_3H_5{\cdot}C_6H_3<\substack{O\\O}>CH_2$. The recently discovered shikimole appears to be identical with safrole. Both are optically inactive. H. C.

Action of Formic Acid on French Terebenthene. By J. Lafont (*Compt. rend.*, **106**, 140—142).—The terebenthene boiled at 155—158°; rotatory power, $[\alpha]_D = -39° 50'$.

2 parts of terebenthene and 1 part of glacial formic acid are gradually mixed, care being taken to avoid a rise of temperature, and the mixture is allowed to remain at the ordinary temperature for some time. Its rotatory power increases considerably. It is then treated with water, and fractionated. The fraction boiling at 135—138°, under a pressure of 40 mm., is more mobile than the original terebenthene; rotatory power, $[\alpha]_D = -69° 25'$; sp. gr. at 0° = 0·9986. It has the composition $C_{10}H_{16},CH_2O_2$, and with dry hydrogen chloride yields formic acid and terpilene hydrochloride. It is violently attacked by nitric acid with formation of resinous products. Potash produces potassium formate and a viscous substance identical with the terpilenols obtained by the action of acetic acid on caoutchouc and terebenthene. The rotatory power of this terpilenol is $[\alpha]_D = -80°$, and it melts at 32°.

The fractions boiling above 145° in a vacuum contain *terpin formate*, $C_{10}H_{16}(CH_2O_2)_2$, which boils at 170—180° and yields potassium formate and terpin when treated with alcoholic potash, besides a viscous, yellowish diterpilene which boils at 205—215°; sp. gr. at 0° = 0·9446; rotatory power, $[\alpha]_D = -14° 15'$.

The first fractions of the original product contain terebenthene with a slightly increased rotatory power, $[\alpha]_D = -41° 32°$, and a mixture of cymene with terpilene boiling at about 178°. In this respect, the action of formic acid is identical with that of acetic acid.

When terebenthene and formic acid in the same proportions are heated in sealed tubes at 100° for 12 hours, treated with water and fractionated, the main product is diterpilene, a viscous, yellowish, optically inactive substance which boils at 205—215°, under a pressure of 40 mm.; sp. gr. at 0° = 0·9404. The first fractions contain terpilene and cymene, with possibly a small quantity of camphene formate.

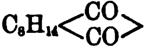
The formation of terpilene formate by the action of formic acid on terebenthene at the ordinary temperature is remarkable, since this compound is not formed by the action of formic acid on terpilene itself. C. H. B.

Yield of Essential Oils by Drugs and Plants. (*Pharm. J. Trans.* [3], 18, 363.)—A table of the percentages of essential oils yielded by 159 species of plants. R. R.

Camphorimide. By A. GUARESCHI (*Chem. Centr.*, 1887, 1354—1355; from *Ann. Chim. Farm.*, 87, 113—122).—A good yield of camphorimide is obtained by heating camphoric acid with 0·3 part of carbamide at 110—120° and finally at 120—125°.

Moine obtained camphorimide and allylcamphorimide by the action of camphoric acid on allythiocarbamide. Camphoric acid and thiocarbamide, or ammonium, or potassium thiocyanate, when fused together, likewise give camphorimide. When potassium thiocyanate is used, carbon oxysulphide is formed.

The camphorimide obtained by these reactions is identical with Laurent's camphorimide from ammonium camphoramate. The specific rotation of a solution of camphorimide in chloroform is $[\alpha]_D = -10·6°$. A silver compound, $C_8H_{14}\!:\!C_2O_2\!:\!NAg$, was formed.

Camphorchlorimide,  $C_8H_{14}{<}\substack{CO\\CO}{>}NCl$, was obtained by dissolving 1 gram of camphorimide in 100 parts of water, adding 1 c.c. of acetic acid, and 10 c.c. of concentrated solution of bleaching powder. From weak alcohol, it crystallises in colourless needles melting at 115·5°. With paratoluidine and aniline, the chlorimide gives a violet-red, with diphenylamine, a green, with pseudocumidine, an orange-coloured product. J. P. L.

Phycophæïn. By F. SCHÜTT (*Chem. Centr.*, 1887, 1379—1380; from *Ber. Bot. Ges.*, 5, 259—274).—Phycophæïn obtained from the various Phæophyceæ (*Fucaceæ*) is identical in composition. The optical properties of phycophæïn consist of a uniform increase of absorption from the red to the blue end of the spectrum. As there are no absorption-bands, the curve is the chief characteristic.

Phycophæïn is easily soluble in hot water, slightly soluble in dilute alcohol, insoluble in ether, carbon bisulphide, benzene, light petroleum, and fixed oils. It is more or less completely precipitated by acids, partially precipitated by soda, and not at all by ammonia or salts of the alkalis. It is precipitated by the salts of the alkaline earths, &c. From its chemical and optical properties, it must, at present, be assigned a position by itself, as it is not directly connected with chlorophyllin or any of the green colouring matters of the chlorophyll-group. J. P. L.

Cyclamin. By G. MICHAUD (*Chem. Centr.*, 1887, 1397; from *Arch. Sci. Phys. Nat.* [3], 18, 198—212).—1 part of cyclamin in 6000 parts of water causes frothing, and in this respect cyclamin surpasses saponin. Cyclamin is more soluble in water at the ordinary temperature than at 70°, but above this temperature the solubility again increases, until at 100° it is about the same as at the ordinary temperature. The rotatory power of cyclamin cannot be determined in watery solution on account of opalescence; in alcoholic solution the author found $[\alpha]_D = -11\cdot40^\circ$. Sachsse states that the rotatory power is $-15\cdot10^\circ$. Mineral acids decompose cyclamin into cyclamiretin and a sugar. The author assigns the formula $C_{36}H_{56}O_{18}$ to cyclamin.

Cyclaminic acid, $C_{36}H_{56}O_{19}$, a weak acid insoluble in water, but easily soluble in alcohol, results from the action of chlorine on a watery solution of cyclamin.

Nitric acid converts cyclamin, cyclamiretin, or cyclaminic acid into *chrysolin*, a nitrogenous, amorphous, and feebly acid substance of the formula $C_{15}H_{21}O_6N$. J. P. L.

Tyrotoxicon. By V. C. VAUGHAN (*Pharm. J. Trans.* [3], **18**, 479—480).—If milk to which some butyric acid ferment has been added, is kept in closely stoppered bottles for eight or ten days, then filtered, and the filtrate, after neutralisation with sodium carbonate, extracted with ether, tyrotoxicon will be obtained in considerable quantity. When a solution in alcohol to which some platinum chloride has been added is evaporated on the water-bath, a violent explosion takes place. The author finds that in this respect tyrotoxicon agrees with diazobenzene compounds, as it does also in giving a similar precipitate with gold chloride. Diazobenzene butyrate and tyrotoxicon were in fact found to be identical in their chemical behaviour and in their physiological effects (described at length in the paper); and from tyrotoxicon obtained from milk, diazobenzene potassium hydroxide, was obtained according to Griess' method. Diazobenzene or some closely-allied substance will probably be found in all those foods which, after putrefactive changes, produce nausea, vomiting and diarrhœa.

Milk or other liquid to be tested for this poison should be kept in well-stoppered bottles, for exposure of the liquid to the air may decompose the tyrotoxicon in a few hours. The filtrate from the milk, or the filtered aqueous extract of cheese, should be neutralised with sodium carbonate, shaken with half its volume of pure ether, and time given for the complete separation. Pure tyrotoxicon being insoluble in ether, the substance probably owes its solubility at this stage to the presence of impurities. The ether is then separated and allowed to evaporate spontaneously, after which the residue may be dissolved in distilled water, and again extracted with ether. A drop of an aqueous solution of the ether residue is then added to a mixture of phenol and pure sulphuric acid, three drops of each, on a porcelain plate, when a coloration, orange-red to purple, will be produced if tyrotoxicon be present. To the remainder of the aqueous solution, an equal volume of saturated aqueous potash is added, and the mixture evaporated on the water-bath. The double hydroxide of potassium and diazobenzene will be formed if tyrotoxicon be present, and may be separated in beautiful six-sided plates, soluble in absolute alcohol, from which it may be precipitated by ether. R. R.

Diastase. By C. J. LINTNER (*J. pr. Chem.* [2], **36**, 481—498; compare Abstr., 1887, 165).—The author has found that diastase prepared from maize by digestion with water, precipitation with alcohol, and subsequent purification by alternately dissolving in water and precipitating with alcohol, has the same diastatic activity and contains the same quantity of nitrogen (10·4 per cent.) as that obtained from barley. Loew's method of purification by precipitation with lead acetate is unsatisfactory, as thereby the diastase loses six-sevenths of its activity. The presence of small quantities of the chlorides of sodium, potassium, and calcium in no way affects the action of diastase on starch solution, but if these substances be present in considerable quantities the conversion into sugar is retarded. Acids and alkalis, cupric sulphate, and probably most salts of the heavy metals, either diminish or completely destroy the activity of diastase. There is at present no evidence to show that two ferments exist in malt, one of which is capable of dissolving starch, whilst the other converts it into sugar; and it must be provisionally accepted that diastase has both these properties. A convenient method of preparing pure maltose consists in treating a solution of starch at ordinary temperatures with precipitated diastase.

G. T. M.

Pyrrolidine. By F. C. PETERSEN (*Ber.*, **21**, 290—293).—The author has purified the pyrrolidine prepared by Ladenburg's method, (Abstr., 1887, 499), by converting it into the bismutho-iodide and decomposing this by distillation with aqueous soda. Thus prepared, pyrrolidine boils at 86·5—88° (compare Abstr., 1885, 1243) and has a specific gravity = 0·879 at 0° and = 0·871 at 10°. The *cadmio-iodide*, $2(C_4NH_9,HI),CdI_2$, crystallises from water in colourless, tabular scales and melts at 200—202°. The nitroso-derivative, $C_4NH_8{\cdot}NO$, is an oil which distils at 214° with partial decomposition and is readily soluble in water.

W. P. W.

β-Picoline. By F. BACHÉR (*Ber.*, **21**, 293—294).—The determinations of the boiling point of β-picoline prepared by Stoehr (this vol., p. 63) and by Hesekiel (Abstr., 1885, 812), do not agree. The author has purified the base obtained by Hesekiel's method by digestion in hydrochloric acid solution with sodium nitrite on a water-bath, and conversion into and crystallisation of its mercurochloride. The base, however, boiled chiefly at 140—142° (corr. 142—144°), whilst fractional crystallisation of the platinochloride prepared from the residue in the distilling flask gave four fractions melting at 187—191°, and corresponding with Stoehr's description of the salt. The research is being continued.

W. P. W.

γ-Picoline and γ-Pipecoline. By A. LADENBURG (*Ber.*, **21**, 285—289).—A commercial lutidine (b. p. = 143—160°) was found to contain 2 : 4 lutidine, β-picoline, and γ-picoline, and the latter was separated from it by the following method. The fraction distilling at 143—147° was converted into the platinochloride, which was washed with ether-alcohol, dissolved in sufficient water to form a 3 per cent. solution, and boiled for many hours in a reflux apparatus in order to convert the picolines into the sparingly soluble, yellow, crystalline platino-salts: the lutidine platinochloride is not affected by this treatment. The platino-salts were then converted into platinochlorides by digestion with concentrated hydrochloric acid in a current of hydrogen chloride, and the γ-salt purified by crystallisation.

γ-Picoline boils at 142·5—144·5° (corr.) and has a sp. gr. = 0·9742 at 0°; the platinochloride melts at 231° with decomposition; the aurochloride forms beautiful, lustrous prisms and melts at 205°; the picrate melts at 167°, and the mercurochloride melts at 128—129°.

γ-Pipecoline, $C_6H_{13}N$, was obtained by the action of sodium on a boiling alcoholic solution of γ-picoline. It is a colourless, hygroscopic liquid which boils at 126·5—129° (corr.) and has a sp. gr. = 0·8674 at 0°. It fumes strongly in the air, has a piperidine-like odour, and is readily soluble in water. The *hydrochloride* is crystalline and readily soluble in water; the *platinochloride*, $(C_6NH_{13})_2,H_2PtCl_6$, crystallises in lustrous prisms, melts at 203° with decomposition, and is soluble in water; the *aurochloride* crystallises in lustreless, yellow needles, melts at 125—127° and is sparingly soluble in water; the *cadmio-iodide* forms white scales and melts at 135°; the *bismutho-iodide* crystallises in characteristic red forms, and the picrate and mercurochloride are crystalline.

The specific gravity of pyridine prepared from the mercurochloride is stated to be 1·0033 at 0°, and a number of instances are cited in which the difference between the molecular volumes of an alkylated pyridine and its hydrogenated derivative approximates to that required by Horstmann's law (Abstr., 1887, 545). W. P. W.

Constitution of Aldehydecollidine. By E. DÜRKOPF and M. SCHLAUGK (*Ber.*, **21**, 294—299).—A comparison between isocinchomeronic acid and the dicarboxylic acid obtained as the final product of the oxidation of aldehydecollidine has established their complete identity, and inasmuch as the collidine has been shown to yield α-picoline (Abstr., 1887, 737), there can be no doubt that its constitution is expressed by the formula C_5NH_3MeEt [Me : Et = 2 : 5]. To explain the formation of this compound from aldehyde and aldehyde-ammonia, the authors suggest that a molecule of aldehyde and a molecule of aldehyde-ammonia react to form the compound $CHO{\cdot}CH{:}CHMe,NH_3$, that simultaneously condensation of the aldehyde and formation of crotonaldehyde also ensues, and that these two products interact under the conditions of the experiment to form aldehydecollidine with the loss of 2 mols. of water. The fractions of lower-boiling point obtained in the purification of aldehydecollidine contain a noteworthy amount of α-picoline, and a small fraction boiling at 160—165° seems to contain β-ethylpyridine, but this is not absolutely certain. W. P. W.

Pseudoquinolineananitrile. By E. LELLMANN and H. REUSCH (*Ber.*, **21**, 397—401).—It has previously been pointed out that quinolineanasulphonic acid and quinolineanacarboxylic acid exist in two modifications (Lellman, Abstr., 1887, 973; Lellmann and Lange, *ibid.*, 737). The authors have now prepared the second modification of the nitrile, the intermediate product. *Pseudoquinolineananitrile*, $C_9NH_6{\cdot}CN$, is obtained by distilling the pseudosulphonic acid with potassium cyanide. It crystallises in slender, colourless needles with 1½ mol. H_2O and melts at 70°. When exposed to air, it loses 1 mol. H_2O and then melts at 74·5°; the remainder of the water is lost on drying over sulphuric acid; the anhydrous substance melts at 89°. It would thus seem that this substance differs from Bedall and Fischer's ananitrile (Abstr., 1882, 413) which presumably is anhydrous (as no reference is made to its containing water of crystallisation) and yields the other modification of the anacarboxylic acid on hydrolysis. Other cases of the existence of these modifications of ana-derivatives are referred to, and further work on the subject is in progress. A. J. G.

Thio-derivatives of Quinoline. By J. Roos (*Ber.*, **21**, 619—630).—*α-Quinolyl mercaptan* (*α-thioquinoline*) $C_9NH_6{\cdot}SH$ [$SH = 2'$] is prepared by heating carbostyril and phosphoric sulphide at 135—145°; it forms yellow plates, melts at 174°, is insoluble in cold, sparingly soluble in hot water, readily soluble in alcohol, ether, benzene, chloroform, carbon bisulphide, and acetic acid. It shows both acid and basic properties and readily forms double salts; it has tinctorial properties, but is not a sufficiently powerful dye for technical purposes. Neither hydroxylamine nor phenylhydrazine react with it.

α-Quinolyl disulphide, $(C_9NH_6)_2S_2$, is obtained by oxidising the mercaptan with hydrogen peroxide; it crystallises in lustrous, white plates, melts at 137°, and is insoluble in alkalis, ammonia, and water, readily soluble in acids and in alcohol, ether, benzene, light petroleum, and chloroform.

α-Quinolyl ethyl sulphide, $C_9NH_6{\cdot}SEt$, is prepared by the action of ethyl iodide on equimolecular proportions of quinolyl mercaptan and sodium dissolved in alcohol, as an uncrystallisable oil which cannot be distilled; it was therefore converted into the *platinochloride*, which crystallises in microscopic octahedrons with 1 mol. H_2O. The *hydriodide*, $C_9NH_6{\cdot}SEt,HI$, is formed by heating the mercaptan with ethyl iodide; it forms pale-yellow crystals and melts at 154°.

γ-Methylquinolyl mercaptan (*α-thiolepidine*), $C_9NH_5Me{\cdot}SH$[$SH : Me = 2' : 4'$], prepared by heating γ-methylcarbostyril with phosphoric sulphide at 140—150°, crystallises in pale-yellow needles, melts at 253°, sublimes at a higher temperature in yellow needles, and is insoluble in water, sparingly soluble in cold alcohol, readily in ether, benzene, chloroform, and carbon bisulphide. It has both acid and basic properties and does not react with hydroxylamine or phenylhydrazine. The *disulphide*, $(C_9NH_5Me)_2S_2$, prepared by oxidation with hydrogen peroxide, forms white plates, melts at 167°, and is readily soluble in alcohol, ether, and benzene, insoluble in alkalis.

γ-Methylquinolyl ethyl sulphide, $C_9NH_5Me{\cdot}SEt$, is an oil; the platinochloride crystallises with ½ mol. H_2O. The hydriodide, obtained by the action of ethyl iodide on the mercaptan, forms long, yellow needles and melts at 214°.

α-Methylquinolyl mercaptan (*γ-thioquinaldine*), $C_9NH_5Me{\cdot}SH$ [$SH : Me = 4' : 2'$], is prepared from γ-oxyquinaldine; it crystallises with 1 mol. H_2O in yellow prisms, which soon turn red on exposure to air, melts at 187°, and is sparingly soluble in cold, moderately soluble in hot water and in alcohol, ether, and benzene.

α-Methylquinolyl ethyl sulphide, $C_{10}NH_8 \cdot SEt$, prepared like the corresponding compounds, crystallises in well-formed, white needles, melts at 56°, is readily soluble in alcohol and ether, insoluble in water, and gives a crystalline platinochloride. A. J. G.

Action of Sulphuric Acid on Quinoline. By G. v. Georgievics *Monatsh. Chem.*, 8, 639—646; compare this vol., p. 296).—When orthoquinolinesulphonic acid is heated with sulphuric acid (7 parts) at 300° for eight hours, paraquinolinesulphonic acid is formed. The yield is 70 per cent. Quinoline is formed as intermediate product.

Orthoquinolinesulphonic acid is obtained when quinoline is heated with sulphuric acid at 220—230°; if the temperature is raised to 240—250°, the para-acid is formed.

Paraquinolinesulphonic acid crystallises in long monoclinic needles; $a : b = 1 \cdot 3514 : 1$; $\beta = 66° 46' 26''$.

Parasulphocinchonic acid (Weidel, Abstr., 1882, 225) is conveniently prepared by heating cinchonic acid with sulphuric acid (6 to 7 parts) at 290—300° for 8 to 10 hours. The whole is poured into water and about three-fourths of the sulphuric acid precipitated with barium carbonate. It is then filtered, extracted with boiling water, and the united filtrates evaporated until a sample of the liquid deposits crystals in one or two hours; after standing 24 hours, these are collected and recrystallised two or three times. The yield of pure acid is more than 40 per cent. of that required by theory. When the acid is fused with potash, a hydroxy-acid is formed identical with that obtained by Weidel (*loc. cit.*), and also with Skraup's xanthoquinic acid (*ibid.*, 223). N. H. M.

Action of Hypochlorous Acid on Quinoline and its Derivatives. By A. Einhorn and R. Lauch (*Annalen*, **243**, 342—362).—Pseudochlorocarbostyril, C_9H_6NOCl, formed by the action of hypochlorous acid on quinoline or of a solution of bleaching powder on quinoline borate, has been previously described by the authors (Abstr., 1886, 370). The chlorine-atom in this compound is easily displaced by hydrogen, yielding carbostyril, but it could not be displaced by groups of atoms. The substance is converted into an isomeride, by the action of absolute alcohol at 100°, or by heating it to a temperature a few degrees above the melting point. The new compound forms rhombic plates and melts at 262—263°; its chlorine-atom cannot be eliminated by the action of moist oxide of silver or by nascent hydrogen. It forms a crystalline potassium salt, and yields chlorisatin on oxidation. As the same compound is formed from 3-chloroquinoline and the same chloroisatin from 3 . 1′ chlorhydroxyquinoline, it is evident that in the intramolecular change which has taken place, the chlorine-atom in the original compound has migrated from the pyridine-ring to the benzene nucleus, forming *parachlorocarbostyril*. A third isomeride resembles the preceding compound, but melts at 106°.

Parachlorocarbostyril hypochlorite, $C_9NH_5Cl \cdot OCl$ [$Cl : OCl = 3 : 1'$], is formed by the action of bleaching powder solution on a solution of parachlorocarbostyril. It is deposited from an acetic acid solution in plates melting at 115°. On exposure to the air, the crystals lose their lustre and the melting point of the substance rises. The substance is deposited from water or ethyl acetate in needles, and melts at 145°. It is much more stable than pseudochlorocarbostyril, but is decomposed by boiling alkalis, forming parachlorocarbostyril.

Anachlorocarbostyril hypochlorite, prepared from metachloroquinoline, crystallises in needles and melts at 155°. It is decomposed by boiling solutions of alkalis, yielding anachlorocarbostyril, melting at 287°.

Paramethylquinoline yields methylpseudochlorocarbostyril,

$$C_9NH_4MeClO\ [Me : Cl : O = 3 : 1' : 2'].$$

This substance melts with decomposition at 120·5°. An intramolecular change takes place when it is dissolved in boiling alcohol, the chlorine-atom migrating to the benzene nucleus, forming methyl chlorocarbostyril.

These results show that quinoline and 3-methylquinoline are converted into unstable pseudochlorocarbostyrils, but ana- and parachloroquinoline yield hypochlorites. Orthochloroquinoline and orthomethylquinoline, under similar treatment, yield dichloro-substitution products. W. C. W.

Action of Phosphorus Pentachloride on Aniline Ethylmalonate and on Orthotoluidine Ethylmalonate. By L. Rügheimer and C. S. Schramm (*Ber.*, **21**, 299—307; compare Abstr., 1887, 738). Chlorethylhydroxyquinoline, [Cl : Et : OH = 2′ : 3′ : 4′], is converted into *ethylhydroxycarbostyril*, [OH : Et : OH = 2′ : 3′ : 4′], by heating with dilute hydrochloric acid at 165°. This is readily soluble in alcohol and acetone, and crystallises from acetic acid in lustrous, well-formed prisms, which lose their lustre on exposure to the air. The alcoholic solution is coloured a dark-yellow on treatment with ferric chloride.

Hydroxyethyltolucarbostyril, [OH : Et : OH = 2′ : 3′ : 4′], melts at 217·5—220° (not 222—223·5°), and is soluble in acetone and acetic acid. Ferric chloride imparts to its alcoholic solution a yellow colour rapidly changing to yellowish-red.

α-Dichlorobutyranilide, $CEtCl_2{\cdot}CO{\cdot}NHPh$, can be obtained from the product of the action of phosphorus pentachloride on aniline ethylmalonate by treating it with aqueous sodium carbonate in excess, heating cautiously on a water-bath, filtering and precipitating with hydrochloric acid. The precipitate is freed from chlorethylhydroxyquinoline by repeated treatment with concentrated hydrochloric acid, and the α-dichlorobutyranilide is purified by solution in aqueous sodium carbonate and subsequent precipitation with hydrochloric acid. It is a white powder which melts at 199—200°, and is converted into α-chlorhydroxybutyranilide-phenylcarbamine by distilling its solution in aqueous sodium carbonate nearly to dryness, adding the distillate to the contents of the flask, and again distilling, the process being repeated several times. Phenylcarbamine is formed during the operation. The author's view of the formation of α-chlorhydroxybutyranilide-phenylcarbamine is thus confirmed, and the formula NPh:CH·O·CEtCl·CO·NHPh is now ascribed to the compound. It is readily soluble in alcohol, less so in light petroleum, and yields phenylcarbamine when boiled with concentrated aqueous potash.

α-Chlorhydroxybutyro-orthotoluide-orthotolylcarbamine, probably $C_6H_4Me·N:CH·O·CEtCl·CO·NH·C_6H_4Me$, is obtained under similar conditions from the product of the action of phosphorus pentachloride on orthotoluidine ethylmalonate. It crystallises in needles, melts at 105—107°, is readily soluble in alcohol, less so in light petroleum, and when heated with sodium carbonate at 130° gives off the odour of phenylcarbamine. W. P. W.

Synthesis of the Homologues of 4′ Hydroxyquinaldine. By M. CONRAD and L. LIMPACH (*Ber.*, **20**, 523—533).—*Methyl orthotolylamidocrotonate*, $C_{12}H_{15}NO_2$, is prepared by keeping a mixture of orthotoluidine and methyl acetoacetate (eq. mols.) for a day; the water which separates is removed, and the oily product which afterwards solidifies is crystallised from alcohol, from which it separates in lustrous prisms melting at 31°. The *ethyl salt* is a slightly yellow oil.

Orthomethyl-γ-hydroxyquinaldine, $C_9NH_4Me_2·OH$ [Me_2 : OH = 1 : 2′ : 4′], is formed together with some orthoditolylcarbamide when ethyl tolylamidocrotonate is quickly heated at 240—250°. It crystallises from water, which dissolves it sparingly, in plates, with 1 mol. H_2O. The anhydrous substance melts at 260—261°, dissolves readily in alcohol, dilute acids, and alkalis, and is almost insoluble in ether, benzene, and chloroform. The *platinochloride* crystallises in light yellow, matted needles, becomes dark at 250°, decomposes completely at 270°, and is readily soluble in boiling water or alcohol.

Methyl paratolylamidocrotonate, $C_{12}H_{15}NO_2$, forms large, lustrous prisms melting at 60·5°, and is readily soluble in ether and alcohol. The *ethyl salt* melts at 29·5°.

Paramethyl-γ-hydroxyquinaldine, $C_{11}H_{11}NO$, obtained together with ditolylcarbamide by quickly heating the ethyl salt just mentioned, crystallises in needles with 1 mol. H_2O; the anhydrous compound melts at 274—275°. The *hydrochloride* dissolves very readily in hot water and crystallises in slender needles; the *platinochloride* crystallises in orange-coloured, lustrous prisms which melt at 228°.

Orthoparadimethyl-γ-hydroxyquinaldine, $C_{12}H_{13}NO$, prepared by heating ethyl metaxylyl-β-amidocrotonate, crystallises in needles with 1 mol. H_2O, melts at 263—264°, and is readily soluble in alcohol, almost insoluble in ether and benzene. The *platinochoride* forms slender, pale-yellow needles, and melts at 282° with decomposition.

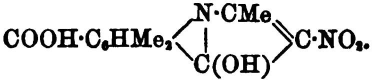
Orthoparadimethyl-γ-chloroquinaldine, $C_{12}H_{12}NCl$, is obtained by treating the hydroxy-derivative with phosphorus pentachloride in presence of phosphorus oxychloride, and afterwards heating the whole at 130° for ½ hour. It crystallises from ether in flat prisms, almost insoluble in water, readily in dilute acids, in alcohol, ether, and benzene, melts at 114°, and boils at 297—298°. The *platinochloride* forms reddish-yellow needles, very sparingly soluble in hot water. When the base is heated with aniline for 10 minutes at 185°, *phenylamidodimethylquinaldine*, $C_9NH_3Me_3·NHPh$ [Me_3 : NHPh = 1 : 3 : 2′ : 4′], is formed;

this crystallises from hot dilute alcohol in prisms melting at 150°. Dixylylcarbamide, obtained in the preparation of dimethylhydroxyquinaldine, melts at 263°.

Methyl cumylamidocrotonate, $C_{14}H_{19}NO_2$, melts at 60·3°; the *ethyl salt* is a viscous, oily substance which when heated at 250° yields condensation products; amongst them *dicumylcarbamide* melting above 300°.

Dicumylcarbamide, $C_{19}H_{24}N_2O$, which is contained in the volatile product obtained by heating ethyl cumylamidocrotonate, crystallises in white, lustrous needles melting above 300°; it is insoluble in the usual solvents.

Trimethyl-γ-hydroxyquinaldine, $C_{13}H_{15}NO$ [$Me_4 : OH = 1:3:4:2':4'$], the non-volatile product obtained by heating methyl cumylamidocrotonate, crystallises in lustrous prisms which sublime at 285° with partial decomposition, but without melting. It is readily soluble in alcohol, sparingly soluble in water. The *platinochloride* separates from alcohol in lustrous prisms which decompose at above 275° without previous fusion. When the base is heated on a water-bath with 10 parts of nitric acid (sp. gr. = 1·4), a violent reaction takes place and a product is obtained which contains, among other substances, *nitrodimethylhydroxyquinaldinecarboxylic acid*,



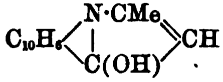
$$COOH{\cdot}C_6HMe_2\left\langle\begin{array}{c}N{\cdot}CMe\\ |\\ C(OH)\end{array}\right\rangle C{\cdot}NO_2.$$

This forms a fine white powder which decomposes at a high temperature without melting. The *sodium salt* crystallises (with 1 mol. H_2O) in long, slender, pale-yellow needles of a satiny lustre.

Ethyl α-naphthylamidocrotonate, $C_{16}H_{17}NO_2$, crystallises in white lustrous needles melting at 45°. When heated at 240°, a violent reaction takes place; the temperature rises to 280° and the whole solidifies.

α-Naphtho-γ-hydroxyquinaldine, $C_{14}H_{11}NO$, separates from its alcoholic solution in groups of needles which partly sublime but do not melt even at 300°. The *nitrate* is rather readily soluble in hot water; the *platinochloride* is a pale-yellow substance, very sparingly soluble in hot water.

Ethyl β-naphthylamidocrotonate, $C_{16}H_{17}NO_2$, crystallises in well-formed prisms melting at 66°, readily soluble in alcohol. When heated at 240°, it behaves similarly to the α-compound.

β-Naphtho-γ-hydroxyquinaldine, $C_{14}H_{11}NO$, crystallises in prisms which do not melt at 300°; it is sparingly soluble in water, more soluble in alcohol. The *platinochlorde* forms a bright yellow, very sparingly soluble precipitate. The constitution of β-naphthohydroxyquinaldine is probably  $C_{10}H_6\left\langle\begin{array}{c}N{\cdot}CMe\\ |\\ C(OH)\end{array}\right\rangle CH$ [$N : C{\cdot}OH = 1 : 2$].

N. H. M.

Syntheses in the Quinoline Series by means of Acetylacetone. By A. Combes (*Compt. rend.*, **106**, 142—145).—2′ 4′

Dimethylquinoline is obtained by dissolving acetylacetoneanilide in concentrated sulphuric acid and heating for a short time on the water-bath. It boils without decomposition at 264—265°.

2′ . 3′ . 4′ *Trimethylquinoline* is prepared by treating methylacetylacetoneanilide in a similar way. It melts at 65° and boils at 285°.

3 . 2′ . 4′ *Trimethylquinoline* is obtained in the same way, from the derivative of acetylacetone and paratoluidine. It forms white crystals, melts at 39—40°, boils at 281—282° without decomposition, and yields a crystalline platinochloride which melts at 220° without decomposing.

1 . 2′ . 4′ *Trimethylquinoline* is obtained from the orthotoluidine-derivative in the same way. It boils at 280° and forms crystallisable salts. The platinochloride melts without decomposition at 255—260°.

C. H. B.

Synthesis of 2′ : 4′ Phenylhydroxyquinoline. By M. Conrad and L. Limpach (*Ber.*, **21**, 521—522).—When ethyl benzoylacetate is heated for several days with aniline, *ethyl β-phenylamidophenylacrylate* is obtained as a thick oil, readily soluble in ether, alcohol, and benzene. This is quickly heated at 250° for a short time; alcohol and some other volatile products distil over, whilst the residue consists of 2′ : 4′ phenylhydroxyquinoline hydrochloride, from which the free base is liberated by means of sodium carbonate. It is identical with the compound prepared by Just (Abstr., 1886, 811). It is probable that most of the 2′ : 4′ phenylhydroxyquinoline-derivatives can be prepared by this method.

N. H. M.

Has Creatinine Basic Properties? By E. Salkowski (*Zeit. physiol. Chem.*, **12**, 211—215).—Creatinine has not the strongly alkaline reaction commonly ascribed to it, but that reaction is dependent on impurities mixed with it, namely, certain constituents of the ash, especially the barium carbonate used in its preparation. The minimal alkaline reaction of the purest possible preparation is also due to a similar slight admixture with ash. 0·113 gram of pure creatinine was dissolved in water, and it was found that a single drop of $\frac{1}{4}$ normal sulphuric acid neutralised the alkaline reaction, and two drops gave an acid reaction; whereas the quantity necessary to neutralise such an amount, had a compound with the acid been formed, would have been 4 c.c. The question was then re-investigated, whether creatinine is able to displace ammonia from ammonium salts. The salt employed was ammonium chloride. In the first place a certain amount of the ammonium chloride solution was distilled, and the ammonia in the distillate estimated colorimetrically by Nessler's reagent. The same amount of the salt solution was then distilled with a known weight of creatinine; and the amount of ammonia in the distillate was found to be much increased, five times as much ammonia being evolved. Control experiments showed that this could not have been yielded by the creatinine itself, nor by the action of the ash of the creatinine on the ammonium chloride; therefore creatinine itself has the action in question. Other nitrogenous substances which form salts, especially the amido-acids, might be expected to act in like manner, but leucine was not found to do so. It is also possible on the other hand that excess of ammonia will decompose creatinine-zinc chloride. On heating an aqueous solution of creatinine-zinc chloride with excess of ammonia, a deposit of zinc oxide is formed; if the boiling is continued until there is no more deposit, the solution is found to be neutral, contains ammonium chloride and creatinine, but only traces of zinc. If it is evaporated to dryness, the residue taken up with alcohol, the alcoholic extract evaporated to dryness, and the residue taken up with water, and zinc chloride solution added, creatinine zinc chloride is again formed. W. D. H.

Creatinine. By G. S. Johnson (*Proc. Roy. Soc.*, **42**, 365—370).—$\frac{1}{20}$th of its volume of a saturated solution of sodium acetate is added to fresh urine, and then $\frac{1}{4}$th of its volume of saturated mercuric chloride. The precipitate of mercuric urate first produced is filtered off, and the liquid left for 48 hours, when a granular precipitate falls, having the composition $4(C_4H_7N_3O,HCl,HgO),3HgCl_2$. It is soluble in hydrochloric acid, insoluble in acetic acid. When moistened with aqueous potash it blackens, and much "compound ammonia" is evolved. By decomposition with hydrogen sulphide, the hydrochloride is obtained, and from this by decomposition by lead hydroxide, the free base, $C_4H_7N_3O$, crystallising in square plates with bevelled edges; an efflorescent hydrate, $C_4H_7N_3O,2H_2O$, can also be obtained, crystallising in long prisms. The aqueous solution of the base is strongly alkaline, has a bitter taste, and gives crystalline precipitates with zinc and mercuric chlorides or picric acid, but none with silver nitrate. It reduces cupric oxide in the proportion of 12 : 10. The average weight passed in 24 hours is 1·7 to 2·1 gram = 1·5 to 1·75 gram glucose. The platinochloride crystallises in orange-coloured prisms, and has the composition

$$(C_4H_7N_3O)_2,H_2PtCl_6 + 2H_2O.$$

A comparative table of various creatinines is given. H. K. T.

Formula of Morphine. By D. B. Dott and R. Stockman (*Pharm. J. Trans.* [3], 18, 708).—After elaborate investigation, Wright decided that the formula of morphine must be at least double the empirical one, that is, it should be $C_{34}H_{38}N_2O_6$; but the authors have failed to obtain confirmation of Wright's views, either from their own experiments or from a repetition of his. They conclude that the formula $C_{17}H_{19}NO_3$ ought to be retained, as it is consistent with all that is known of the alkaloïd, and they suggest that probably the substances with which Wright operated were mixtures. R. R.

Morphine Hydrate. By D. B. Dott (*Pharm. J. Trans.* [3], 18, 701).—The author finds that, contrary to the statements of all the authorities, a temperature below 100° suffices to deprive morphine of all its water of crystallisation. He infers from his results that the hydrate has the formula $8C_{17}H_{19}NO_3 + 9H_2O$, and not $C_{17}H_{19}NO_3 + H_2O$ as usually stated. R. R.

Derivatives of Cinchonine. By E. JUNGFLEISCH and E. LÉGER (*Compt. rend.*, **106**, 68—71).—The isomerides of cinchonine previously described (this vol., p. 380) are separated by precipitation with soda, washing the precipitate, and treating it with ether.

The ethereal solution is heated to expel ether, and neutralised with hydrochloric acid. After some days, cinchonigine hydrochloride crystallises out, and a fresh crop of crystals can be obtained by concentrating the mother-liquor. If the mother-liquor is then precipitated with soda, the precipitate extracted with ether, the ether expelled, and excess of colourless hydriodic acid added, a yellow, crystalline precipitate of cinchoniline dihydriodide is obtained. After separation of these two alkaloïds, the liquid contains a small quantity of a base which has yet to be examined.

The portion of the original precipitate insoluble in ether, is dissolved in strong, boiling alcohol, distilled until crystals separate in the hot liquid, and mixed with an equal volume of water. After standing overnight, the precipitate is dissolved in water containing succinic acid, and the solution concentrated, when it deposits needles of cinchonibine succinate, a further quantity of which is obtained by again concentrating. The mother-liquor is precipitated with soda, and the precipitate dissolved in colourless hydriodic acid to form a neutral solution, which after some time deposits crystals of cinchonifine hydriodide.

The dilute alcoholic solution is distilled, and the aqueous residue neutralised with hydrochloric acid, and filtered whilst boiling. The filtrate deposits crystals of α-hydroxycinchonine hydrochloride. When no more crystals of this compound can be obtained from the concentrated mother-liquor, it is neutralised with soda, mixed with acetone, and the precipitate of β-hydroxycinchonine washed with acetone.

C. H. B.

Action of Oxalic Acid on Cinchonine in Presence of Sulphuric Acid. By CAVENTOU and C. GIRARD (*Compt. rend.*, **106**, 71—73).—Cinchonine when heated at 125—130° with oxalic acid and monohydrated sulphuric acid for several days is partly converted into two bases, one of which is soluble in both ether and benzene, whilst the other is soluble in ether but insoluble in benzene. The first has the same composition as cinchonine, but forms large crystals which retain benzene unless heated at 100°; it dissolves in acetone, chloroform, and methyl, ethyl, and amyl alcohols. It melts at 125°, and its lævorotatory power in a 1 per cent. alcoholic solution is $[\alpha]_D$ −58° 3′. With potash, it yields quinoline and pyridine-derivatives. The hydrochloride is soluble in water, and crystallises readily, its rotatory power is $[\alpha]_D = -68° 28'$. The platinochloride is orange-yellow, and dissolves in hot water; the sulphate crystallises well, but is very soluble; the chromate is orange, and somewhat soluble in water, differing in this respect from cinchonine chromate. The physiological action of this base is similar to that of cinchonine, but more energetic.

The base insoluble in benzene and the other products soluble in ether have not yet been examined. C. H. B.

Hygrine. By R. Stockman (*Pharm. J. Trans.* [3], **18**, 701).—Hygrine exists in only a very minute amount in dried coca leaves, probably because it is volatilised in the process of desiccation, but from an alcoholic extract of the fresh leaves, the author obtained it in relatively larger quantity, as a brown oily liquid, with a characteristic smell and burning taste, and an alkaloïdal reaction. It is an extremely irritating substance, and a drop placed on the tongue causes a burning sensation. When a drop mixed with water is injected under the skin of a frog, the animal dies after a time, and all the muscles, bowels, and serous membranes are found studded with minute hæmorrhages. Hence hygrine must be carefully eliminated from all therapeutic preparations of cocaïne. R. R.

Cholic Acid. By F. Mylius (*Zeit. physiol. Chem.*, **12**, 262—266; compare Abstr., 1887, 606, 982).—The author repeats in detail his method of preparing cholic acid; it crystallises from absolute alcohol in tetrahedra of the composition $C_{24}H_{40}O_5,C_2H_6O$. Much cholic acid remains in solution in the alcohol; he considers it possible, although he has not worked definitely at the subject, that a form of cholic acid exists which does not yield a crystalline compound with alcohol. The formula $C_{24}H_{40}O_5$ for cholic acid is that originally ascribed to it by Strecker. He criticises the work of Latschinoff on this subject, who has recently (this vol., p. 303) given $C_{25}H_{42}O_5$ as the formula for cholic acid. He considers that the aniline and toluidine cholates are unsuitable compounds on the analysis of which to found a formula, and also considers it improbable that such compounds as $C_{25}H_{42}O_5 + \frac{1}{8}H_2O + \frac{7}{8}C_2H_6O$, or $C_{25}H_{42}O_5 + \frac{1}{8}H_2O + \frac{7}{8}C_6H_6O$ exist.

W. D. H.

Colour Reactions of Proteïds. By E. Salkowski (*Zeit. physiol. Chem.*, **12**, 215—222).—A part of the proteïd molecule belongs to the aromatic group of compounds, and it is on the presence of aromatic radicles in proteïds that the well-known colour reactions given by those substances depend. By the putrefaction of proteïds, aromatic substances are formed, which fall into three groups: (1) the phenol-group, including tyrosine, aromatic hydroxy-acids, phenol, and cresol; (2) the phenyl-group, which contains phenylacetic and phenylpropionic acid; and (3) the indole-group, of which indole, scatole, and scatolecarboxylic acid are the most important members. Whether all three groups exist preformed in the proteïd molecule, or whether that molecule contains only one aromatic group, and the others are easily derived from this one on decomposition (Maly), matters little in a solution of the question investigated, namely, on which of the groups do the colour reactions depend. These colour reactions were tried with each of the substances enumerated, and the following were the results obtained:—

1. *Millon's Reaction.*—This does not occur in presence of sodium chloride. Kühne considers that the reaction is due to tyrosine; O. Nasse that it is dependent on those benzene-derivatives in which only one atom of hydrogen is displaced by hydroxyl. In this research, it was found to be given only by substances enumerated under the first group. The precaution must be taken to prepare the reagent as

originally described. Gelatin also gives the reaction faintly; the purest gelatin yields traces of phenol (Weidel and Ciamician, *Ber.*, **14**, 1009).

2. *The xanthoproteic reaction* depends without doubt on the formation of nitro-derivatives. The trinitro-albumin and oxytrinitro-albumin of Löw (this Journal, 1872, 1028) are very doubtful chemical units. Nencki and Sieber (Abstr., 1885, 826) have obtained paranitrobenzoic acid by the action of fuming nitric acid on dry albumin, but as this acid is colourless, it cannot be that which gives the yellow colour. The substances enumerated in the first group give the reaction strongly; those in the third group give it well, but not so well as those in the first group; indole gives it feebly, except when fuming nitric acid is used; and the substances in the second group do not give it at all, or exceedingly faintly. The xanthoproteic reaction can be used to determine peptone or perhaps albumin quantitatively in an approximate manner. It is much better than the violet or pink tint caused by copper sulphate and potassium hydroxide, as proposed by Schmidt-Mülheim, for three reasons: (1) gelatin and gelatin peptone do not give the xanthoproteic reaction; (2) the shade as well as the intensity of the colour varies greatly in the copper sulphate test; and (3) the colour of the original solution does not interfere with this test, except in very exceptional cases.

3. *The Adamkiewicz Reaction.*—This test is given by all proteïds, including albumoses and peptones, but not by gelatin or its peptones. It is not, however, a certain test, and in the case of albumoses and peptones is given only with concentrated solutions. It is given only by the aromatic substances of the third (indole) group, and especially by scatolecarboxylic acid. The addition of a minimum quantity of potassium nitrite intensifies the colour, as it does also in solution of proteïds; a further addition of that salt turns the purple colour to red.

4. *The colour reaction with strong hydrochloric acid* (Liebermann, Abstr., 1887, 1150) is not given by any of the aromatic substances enumerated. W. D. H.

Albumoses and Peptones. By R. NEUMEISTER (*Zeit. Biol.*, **24**, 267—271).—In a former article (Abstr., 1887, 285), the author has shown that deutero-albumoses are more allied to peptones than the primary albumoses (proto- and hetero-albumose), not only aetiologically but also in their chemical reactions. Deutero-albumose is for instance not precipitated, as are the primary albumoses, by saturation with sodium chloride, nitric acid in the absence of salt, nor by cupric sulphate. To this list, must now be added saturation with ammonium sulphate for one variety of deutero-albumose; the deutero-albumose which is formed from hetero-albumose, and also that formed from anti-albumid, is completely precipitated by saturation with ammonium sulphate; but the form of deutero-albumose (probably hemi-deutero-albumose) which is formed from proto-albumose, is to a certain extent soluble in saturated solutions of ammonium sulphate, even in the presence of acetic or sulphuric acid.

The different albumoses may be prepared in a pure state as follows:

—"Witte's peptone" is completely dissolved by prolonged digestion with 3 per cent. hydrochloric acid at 40°; the solution is then neutralised, and saturated with sodium chloride; the precipitate which contains the two primary albumoses is redissolved, and hetero-albumose precipitated by dialysing out the salt from the solution. The proto-albumose remains in solution with a certain amount of deutero-albumose, from which it is separated by saturating the boiling solution with ammonium sulphate; the precipitate of proto-albuminose is collected, redissolved, and the saturation repeated until the filtrate does not give the biuret reaction. Its solution is then dialysed, concentrated, alcohol added, and the resulting precipitate washed with ether and dried in a current of dry air. The hetero-albumose is purified by prolonged washing with cold water, in which it is, however, not so insoluble as has been hitherto supposed (this solubility increases at a temperature of 40°); it is then redissolved, precipitated by ammonium sulphate, and the rest of the process is the same as with proto-albumose.

The deutero-albumoses are present in the filtrate after the precipitation of the primary albumoses; they are separated from the peptone by means of acetic acid saturated with ammonium sulphate; the precipitate of the deutero-albumoses is dissolved in water, boiled, and saturated with ammonium sulphate; a certain amount of the hemi-deutero-albumose remains in solution; the precipitated deutero-albumose is redissolved and the operation repeated, until a precipitate is obtained which is wholly soluble in water, and on saturating which with ammonium sulphate no proteïd is left in solution; this deutero-albumose is then freed from salt and purified as in the other cases. The hemi-deutero-albumose is obtained by concentrating the filtrates.

W. D. H.

Nucleïn from Yeast: Artificial Preparation of Nucleïn from Albumin and Metaphosphoric Acid. By L. Liebermann (*Ber.*, 21, 598—600).—The results here detailed seem to show conclusively that the nucleïns are compounds of albumins with metaphosphoric acid. When yeast nucleïn is extracted with cold dilute nitric acid, metaphosphoric acid goes into solution, whilst the residue no longer gives the characteristic reactions of nucleïn. On the other hand, the precipitate obtained by adding metaphosphoric acid to a solution of egg albumin, cannot be distinguished from the nucleïns either in composition or reactions. It is strange that this precipitate, so well known in testing for albumin, should never have been investigated.

A. J. G.

Resistance of Hæmoglobin towards different Decomposing Agents. By F. Krüger (*Zeit. Biol.*, 24, 318—335).—The hæmoglobin of different animals differs in solubility, in the readiness with with it crystallises, and in crystalline form. Körber (*Inaug. Dissert.*, Dorpat, 1866) stated that hæmoglobin differs also in the readiness with which it is decomposed by such reagents as acetic acid and sodium hydroxide. He published tables of numerous comparative observations on the resistance to decomposition of the hæmoglobin of different animals. He found that the absorption-bands of hæmoglobin of the dog and man disappeared within a minute after the addition of these reagents, whereas in that of herbivorous animals the bands did not completely disappear for several hours when similarly treated. He obtained solutions of hæmoglobin of approximately equal strength by diluting the defibrinated blood with water, till it assumed a standard tint. Körber's results have been considerably criticised (for instance, by Preyer, *Die Blutkrystalle*, Jena, 1871, p. 61), as his experiments were not made with pure hæmoglobin, but in the presence of the other constituents of the blood.

The present research was undertaken with a view of testing the same matter similarly, but accompanied by control experiments with pure hæmoglobin; the hæmoglobin was estimated by means of Hüfner's spectrophotometer (Abstr., 1887, 1126). The blood crystals were dissolved in a 0·1 per cent. solution of sodium hydroxide instead of distilled water. The hæmoglobin of the dog and horse only were examined as examples of the pigment, in which Körber states the difference in their resistance to decomposition is very marked. The time between the addition of the reagent and the disappearance of the absorption-band was noted. The following gives in tabular form an example of the kind of experiment performed and results obtained:—

Time in Minutes in which a 10 *per cent. Solution of Acetic Acid and Sodium Hydroxide respectively caused the Decomposition of* 0·05 *gram of Hæmoglobin in Solution.*

	Amount of acetic acid added in c.c.	Time.		Amount of soda added in c.c.	Time.	
		Dog.	Horse.		Dog.	Horse.
Blood and water ...	0·5	64	350	0·25	78	380
” ...	1·0	24	219	0·50	10	104
” ...	1·5	10	111	1·00	1·5	54
Hæmoglobin after one crystallisation dissolved in water	0·5	65	350	0·25	77	310
	1·0	25	189	0·50	11	104
	1·5	12	106	1·00	1·25	44
Hæmoglobin after two crystallisations dissolved in water	0·5	65	350	0·25	79	310
	1·0	24	189	0·50	11	104
	1·5	12	106	1·00	1	44

That it is the hæmoglobin itself and not any other constituent of the blood that causes this difference was shown by taking the blood corpuscles of one animal, and by the use of a centrifugal separator ridding them of serum, and then adding the serum of the other animal to the corpuscles. The hæmoglobin under these circumstances retained its characteristic resistance to the reagents used.

The conclusions finally drawn from such experiments are:—(1.) That Körber's statement regarding the great difference in the power with which the hæmoglobin of these two animals resists the decomposing action of acetic acid and sodium hydroxide is perfectly correct, and that moreover Körber's method is one which leads to correct results. (2.) That this difference is due to a difference in the chemical composition of the hæmoglobin itself. (3.) The difference between the resistance of the two forms of hæmoglobin examined increases with the quantity of the reagent used. (4.) Within the limits of the quantities used in experiments, such as the one given here in detail, sodium hydroxide is the more powerful reagent of the two.

W. D. H.

Activity of Reduction of Oxyhæmoglobin. By A. HENOCQUE (*Compt. rend.*, **106**, 146—147).—An account of the variations in the activity of reduction of oxyhæmoglobin in various diseases under the influence of various drugs.

C. H. B.

Physiological Chemistry.

Rapid Absorption of Carbonic Anhydride from Expired Air. By A. D'ARSONVAL (*Compt. rend. Soc. Biol.*, **4**, 750—751, and 751—753).—The difficulty of wholly absorbing all the carbonic anhydride from expired air is completely overcome by submitting the air to a fine spray of the potash solution. This is accomplished with an apparatus which is essentially a spray-producer. The spray is produced by suction, and the expired air drawn through a tube with which the spray-producer is concentric. An apparatus is also described for permitting a person to breathe in a limited atmosphere of constant composition, and for registering the absorption of oxygen, and the disengagement of carbonic anhydride.

J. P. L.

Absorption of Carbonic Anhydride, and Graphic Record of the Carbonic Anhydride Expired. By M. HANRIOT and C. RICHET (*Compt. rend. Soc. Biol.*, **4**, 753—754).—Complete absorption of the carbonic anhydride is effected by passing the air through a burette 1½ metres long filled with broken glass over which potash flows. A method is explained for graphically recording the oxygen absorbed and carbonic anhydride exhaled.

J. P. L.

Formation of Ammonia in the Pancreatic Digestion of Fibrin. By E. STADELMANN (*Zeit. Biol.*, **24**, 261—266).—Hirschler (Abstr., 1886, 726) has stated that small quantities of ammonia are formed during the pancreatic digestion of fibrin; but as in his experiments the fibrin that was used had not been previously boiled, and the mixtures were not thymolised or otherwise rendered antiseptic, his results are not considered satisfactory. In the present research, such antiseptic measures were adopted, and putrefaction entirely prevented. Some of the mixture before digestion was distilled with sodium carbonate, and the distillate titrated with sulphuric acid; a small amount of ammonia was present, but this was not increased even after digestion had gone on for 10 days.

The conclusion was therefore drawn, either that no ammonia is formed, or that if it is, it is combined in such a manner, that distilling with sodium carbonate does not drive it off.

To solve this question, the following method was adopted; the digestive mixture was filtered; the filtrate distilled, and the distillate received in hydrochloric acid; to the residue, a few drops of acetic acid were added, then excess of *magnesia usta*, and it was again distilled, and the distillate collected as before. Both filtrates were evaporated and treated with platinic chloride; the resulting precipitates washed with alcohol and ether, ignited, and the ammonia calculated from the weight of the platinum residue.

By this method, it was found that Hirschler's statement was fully confirmed as to the occurrence of ammonia; although whether it is present as an ammonium salt, or in some hitherto unknown organic compound, there is not sufficient evidence to say. W. D. H.

Influence of Phenylacetic Acid on Proteïd Metabolism. By E. Salkowski and A. Kotoff (*Zeit. physiol. Chem.*, **12**, 222—226).—Researches were made on dogs:—the animal first received 50 c.c. of milk only daily for a few days, and then for some days with the addition of 2 grams of sodium phenylacetate dissolved in water. The animals generally died in three or four days after this compound was given.

Taking an average of the five series of researches, the following numbers were obtained relating to the amount of nitrogen and sulphuric acid passed in the 24 hours:—

	Daily average.		
	N.	Total SO_3.	Combined SO_3.
Phenylacetic acid not given ..	1·254	0·120	0·038
„ „ given	1·921	0·256	0·028

The decomposition of proteïd is thus increased, though why the amount of sulphuric acid is increased in such greater proportion than the nitrogen it is at present impossible to say. The decrease in the combined sulphuric acid (ethereal hydrogen sulphates) is doubtless due to the antiseptic action of the compound administered. As was pointed by Müller (*Zeits. f. Klin. Med.*, **12**, 19), the absolute quantity of ethereal hydrogen sulphates in the urine is a much more correct measure of the amount of putrefaction going on in the intestine, than the relation between those sulphates, and the normal sulphates of the urine. W. D. H.

The Output of Chlorides in its Relation to Metabolism. By A. Kast (*Zeit. physiol. Chem.*, **12**, 267—284).—The automatic regulation of the discharge of chlorides, according to Forster (*Zeit. Biol.*, **9**, 297), depends on the decomposition of proteïds; the "circulating proteïds" (Voit) which are in combination with much salt being decomposed before the "tissue proteïds," which are comparatively poor in the amount of salt associated with them. This view is supported by Röhmann (*Zeit. klin. Med.*, **1**), among others, who points out that the clinical facts observed in fever, especially in pneumonia, with regard to the diminution of chlorides in the urine, fully bear it out.

As a result of the present researches, this theory must, however, be modified. The chief observations made are as follows. Chloroform poisoning is followed by an increase of the amount of chlorine in the urine (see Abstr., 1887, 612), and this is accompanied by the presence of abundance of biliary colouring matter in that secretion. In chronic chloroform poisoning, the total metabolism that ensues is diminished, and the animal gains weight.

Starvation in animals previously deprived of chlorides produces an increase in the chlorides excreted (Forster).

Removal of blood from a dog produced a considerable diminution of the chlorides excreted for the four days following the venesection. The diet of the animal in this and similar experiments was constant. This coincides with what is known clinically with regard to the diminution of chlorides in the urine after hæmorrhages in man. The influence of carbonic oxide was next investigated; in normal animals, and in those who have been previously saturated with a large excess of chlorides in the diet, carbonic oxide poisoning was followed by lessening of the chlorides excreted; whilst in those which had been previously deprived of chlorides, it produced an increase of the total chlorides of the urine. The minimum of chlorides in the first case was reached a few days after the poisoning; and the less chlorides in the urine the more strongly did that secretion reduce Fehling's solution. If Forster's explanation of the excretion of chlorides is correct, it must also be supposed that under certain conditions the reverse is also true; namely, that the "organ-albumin" contains more salt than the "circulating-albumin." Phosphorus poisoning was found to produce abundant destruction of proteïd with rise of the daily nitrogen in the urine, but a diminished quantity of chlorides.

In view of the appearance of biliary colouring matter in the urine of chloroform narcosis, it was thought possible that some relation might exist between the destruction of red corpuscles and the amount of chlorides in the urine. Bunge (*Zeit. Biol.*, **12**, 191) has shown that sodium chloride is a constant constituent of red blood corpuscles. With a view to testing this opinion, pyrogallol was administered to dogs; this produced blood-tinted urine, albuminuria, and greatly increased chlorides in the urine; this corresponds with the destructive influence of this drug on the red corpuscles. The administration of toluylenediamine produces similar result, but is more trustworthy as it produces no albuminuria. Albuminuria in Bright's disease is, however, not necessarily associated with an increased discharge of chlorides.

The conclusion is therefore drawn that there are two distinct factors concerned in regulating or altering the amount of chlorides in the urine; first, proteïd metabolism, to which the output of chlorides is usually in the inverse ratio, and secondly, disintegration of red blood corpuscles, to which it stands in a direct ratio. That when, moreover, the two processes occur simultaneously, the final result depends on which of them it is which preponderates. W. D. H.

Fate of Pyridine in the Organism. By O. DE CONINCK (*Compt. rend. Soc. Biol.*, **4**, 755—756).—His (*Archiv Expt. Path. Pharm.*, **22**,

253) states that pyridine acetate when given by the stomach to dogs does not pass through unchanged, but appears in the urine as picoline, C_6H_7N, of which he prepared the platinochloride and aurochloride.

This is contrary to the author's experience. In a series of experiments which he made in conjunction with Bochefontaine in 1884 with the hydrochloride, pyridine was always secreted unchanged, at least the greater part, in urine, saliva, and breath. The discrepancy might possibly be explained by assuming the addition of a CH_3-group to the pyridine molecule as a result of the decomposition of the acetate in the body. J. P. L.

Nutritive Value of Vegetable Proteïds compared with that of Animal Proteïds. By J. Rutgers (*Zeit. Biol.*, **24**, 351—381).—These experiments were carried out in human beings. Tables are given of the diets employed, at one time containing animal food, at another being an almost exclusively vegetable diet. In all the constituents of the food, the nitrogen, fat, extractives free from nitrogen, sugar, and alcohol were estimated; and the urine and fæces were daily examined, the nitrogen especially being estimated; simultaneous observations were made on the body-weight. The conclusions that are drawn from the results obtained may be thus summarised:—

Vegetable proteïds containing an equal amount of nitrogen can be substituted for the animal proteïds which were used without the nitrogenous balance of the body being disturbed. Beans and peas load the intestinal tract very much, both in respect of their solid constituents and of the gases formed from them; meat and rice have not this disadvantage. This and other contra-indications of a similar nature would render an exclusively vegetable diet undesirable. The acidity of the stomach and also that of the urine is much smaller when the diet is exclusively vegetable than when a mixed diet is taken.

Milk, if it is not taken as the exclusive means of nutrition, is in adults also very completely digested. The questions of the difference in cost of the two diets was found to be regulated only by the cost of heating the oven.

The mean values given by Moleschott as the daily amount of nutriment necessary were not found to be too low for the climate in which the experiments were carried out (Holland). Kjeldahl's method of estimating nitrogen was found to be the best not only for urine and milk, but for fæces also. The method of Pflüger and Bohland for estimating quickly and approximately the nitrogen in human urine yields, especially when the urine is rich in urea, better results than the improved Liebig's method. W. D. H.

Cellulose in the Nutrition of Herbivorous Animals. By W. v. Knieriem (*Zeit. Biol.*, **24**, 293—305).—In a paper by Weiske and others (Abstr., 1886, 728), the conclusion was drawn that cellulose does not economise the decomposition of proteïd, which was precisely the opposite conclusion to that which v. Knieriem, from his former experiments, arrived at (Abstr., 1885, 916). The present paper takes up the subject again, the author reiterating his former views, and criticising the methods, results, and conclusions of Weiske.

W. D. H.

Physiolgical Action of Albumoses and Peptones. By R. NEUMEISTER (*Zeit. Biol.*, **24**, 272—292).—The fate of the products of digestion of proteïds has been the subject of researches by Maly, by Plósz and Gyergyài, by Adamkiewicz and others. Schmidt-Mülheim (*du Bois Reymond's Archiv*, 1880, 33) thought that the products of digestion were absorbed as such, and in the blood became quickly transformed into albumin. An injection of so-called peptone (really albumoses and peptones) into the circulation, vanished as such in a few minutes, and was not observed in the urine; this did not occur when "peptone" was mixed with shed blood. After abundance of proteïd food, small quantities of "peptone" were found in the circulating blood.

Hofmeister (*Zeit. physiol. Chem.*, 1881, 127) found, on the other hand, that injection of "peptone" into the circulating blood was followed by its rapid disappearance from the blood and appearance in the urine. But it as quickly disappears if the quantity injected is sufficient to so lower the blood pressure as to suppress the secretion of urine altogether. He considers that it collects in certain organs, liver, kidneys, &c., under these circumstances. He was able sometimes to discover peptone in the circulating blood during digestion, but supposes that ordinarily it enters into combination with the white blood corpuscles and so escapes detection.

In the present paper it is shown that the methods used by the investigators just quoted, for the identification of peptones is untrustworthy; the method of heating, after acidifying to remove other proteïds, and then calling the still soluble proteïd, "peptone," if it gives the biuret action, is a method which in reality leads to the formation of small quantities of primary albumose, as heating with acid is one means of obtaining these hydration products of proteïds. Milk is taken as an example of a substance in which such artificial products have been described under the name of peptone, hemialbumose, lactoproteïn, &c., by various observers as normal constituents of that secretion. Pus also, which is generally said to contain peptone, was found by improved methods to contain none. These improved methods are as follows:—First, the liquid is precipitated by alcohol; the proteïd precipitate is allowed to remain under absolute alcohol for some weeks, by which time all proteïds but albumoses and peptones are rendered insoluble; the albumoses and peptones can then be removed by extracting the precipitate with water, and identified in solution by their characteristic tests. Peptone and one form of deutero-albumose could be identified in the blood by first receiving it into a solution of ammonium sulphate to prevent coagulation; then dissolving the corpuscles by adding ether; removing the ether; and saturating with ammonium sulphate and filtering; the filtrate would contain deutero-albumose and peptone if present. The lymph, urine, and other fluids can be similarly investigated. It was found that peptones or albumoses never (or only in the merest traces) occurred in the blood or lymph, even when the most energetic digestion of proteïds was going on in the alimentary canal. It was found that injection of albumoses or peptones or both into the circulation was followed by their rapid and complete disappearance therefrom and appearance in the urine within 10 minutes, both in the dog and rabbit; but they also disappear when the ureters are tied. There was no rise of temperature as described by Ott and Collmar (*Med. News*, 1887, February 19). In the dog, it was found that the albumoses, after the injection, underwent hydration before they appeared in the urine; the primary albumoses appearing mostly as deutero-albumoses, and the deutero-albumoses as peptones. This occurred in the urine when it was acid, neutral, or alkaline, and could not be due to digestion by the pepsin contained in the urine, when the latter remained in the bladder. Albumoses even when mixed with acid urine underwent no such change; the large percentage of salts present, and the fact that the acidity is not due to free acid would prevent this. Contact of the albumoses with freshly-drawn blood, or with fresh organs such as liver or kidney, also caused no change in them. The view is advanced that they are digested by the pepsin secreted by the kidneys in the urinary tubules where there is momentarily a formation of free acid. In the rabbit, no such change occurs; the urine contains no pepsin in this animal, and the albumoses injected into the circulation are secreted as such.

W. D. H.

Physiological Action of the Products of Incomplete Combustion of Illuminating Gas. By N. GRÉHANT (*Compt. rend. Soc. Biol.*, 4, 779—780).—To determine the action of the products of the incomplete combustion of illuminating gas, a dog was placed for two hours in a chamber of 12 cubic metres' capacity, in which a Bunsen burner burning at the bottom was also placed.

A comparison of the gases of the blood taken from the carotid artery, before and after the experiment, showed that the oxygen of the original blood was almost wholly displaced by carbonic oxide.

J. P. L.

Action of Ethylene Chloride on the Cornea. By R. DUBOIS and P. ROUX (*Compt. rend. Soc. Biol.*, 4, 584—585).—With the object of establishing some relation between chemical constitution and physiological action, the authors have commenced the study of the chlorine-derivatives of ethane, many of which possess anæsthetic properties. The first compound they have experimented with is ethylene chloride, which is found to have a remarkable action on the cornea.

If a dog is anæsthetised for one hour by inhalation of ethylene chloride, or if the compound is injected subcutaneously, both corneas, especially if the anæsthetising is repeated after the lapse of 24 to 36 hours, become opalescent and of a bluish-white tint, which give to the animal a strange appearance, the curves of the cornea become especially exaggerated in the vertical meridian, where it is easy to show astigmatism. The bluish-white tint and the abnormal prominence of the cornea recall a double symmetrical opaque anterior staphyloma. This experimental lesion is permanent.

Operation for glaucoma was successfully performed on one of the animals; the eye operated on remaining transparent whilst the other became opaque; the cornea is the only part of the eye which appears to be affected.

J. P. L.

Pigments of Melanotic Sarcomata. By K. A. H. Mörner (*Zeit. physiol. Chem.*, **12**, 229—240).—Nencki (*Arch. exp. Pathol. Pharm.*, **24**, 27) has criticised the previous publication of the author on this subject (Abstr., 1887, 168). The present reply to this criticism points out that in the previous paper it is distinctly stated that the analyses given refer to two different pigments, one soluble and the other insoluble in acetic acid, and not to one only as Nencki has supposed.

The author also shows that in Nencki's analyses very great differences occur, and that in some cases the percentages are incorrectly calculated. W. D. H.

Therapeutic Substitutes for Chrysarobin. By C. Liebermann (*Ber.*, **21**, 447—452).—The analogy of the leuco-derivatives of the anthraquinone-dyes (this vol., p. 492) to chrysarobin, the active principle of Goa powder, suggested that the therapeutic action would be similar. This has proved to be the case, as it is found that they will also cure those skin diseases for which chrysarobin is at present employed. They are, therefore, being made on the commercial scale under the name of "*anthrarobins*;" the term *anthrarobin* being more particularly applied to the reduction product from commercial alizarin. The reduction on the large scale is best effected by means of zinc-dust and ammonia. The activity of anthrarobin is reported to be about equal to that of chrysarobin, but more intense than that of pyrogallol; anthrarobin has the advantage that it does not produce inflammation of the skin.

The author is inclined to attribute the therapeutical activity of both chrysarobin and the anthrarobins to their great affinity for oxygen. A. J. G.

Urea and Total Nitrogen in Human Urine. By W. Camerer (*Zeit. Biol.*, **24**, 306—317).—Of every 100 grams of nitrogen obtained from urine, 90 are on the average derived from urea and ammonia; and the remaining 10 from other nitrogenous constituents called extractives. The object of this research was to determine the relation between these two sources of nitrogen under certain conditions. The total nitrogen was estimated by the Varrentrapp-Will method, and the nitrogen from urea by Hüfner's hypobromite method; the small amount of nitrogen yielded by uric acid and creatinine on treating urine with hypobromite was not taken into account, so that the percentage differences in the tables given are a little too small.

For 15 days, the total urine in each 24 hours was collected, its quantity measured, its specific gravity taken, and the nitrogen in it estimated by the two methods. The average of the results of the 15 days, the average of those of the seven of the 15 days when the total percentage of nitrogen was above the average, and the average of those of the remaining eight days when it was below the average, are given in the following table:—

		Average results per diem		
		For the fifteen days.	For the seven days in which the average was exceeded.	For the eight days in which the average was not reached.
Specific gravity		1·016	1·018	1·014
Quantity in c.c.		1840	1488	2147
Total nitrogen		16·06	15·77	16·31
Nitrogen from urea		14·15	14·13	14·17
Total nitrogen	per cent.	0·873	1·06	0·76
Nitrogen from urea		0·769	0·95	0·66
Difference		11·9	10·4	13·1

From this it appears that the increase of the total quantity of urine excreted is accompanied by diminished specific gravity, and that the excretion of extractives is increased both absolutely and proportionally to the total of nitrogenous substances in the urine; the total quantity of nitrogen from extractives in the group of seven days averaging 1·64 gram, and in the other group 2·14. A second series of observations was made to determine the influence of proteïd food on the output of both sources of nitrogen. The experiment was carried out on four persons, each of whom partook of one meat meal in the 24 hours, and whose urine was collected at intervals of three hours. Details similar to those enumerated in the previous experiments are tabulated, and the general results are the following:—The increase in both kinds of nitrogen commences almost immediately after the digestion of the proteïd food; the nitrogen derived from urea reaches its maximum in from 7 to 10 hours, whilst that derived from the extractives is greatest in the four first hours after the commencement of the meal. The percentage difference is greatest during the first three hours and smallest 12 hours after the meal. The quantity of urine is smallest during the first four hours, and greatest from 7 to 10 hours after the meal; the most concentrated urine is thus accompanied by the secretion of the maximum of extractives, which is the opposite to the general result obtained from the first series of experiments.

From the large number of experiments performed, it is found that on the average for every 100 grams of nitrogen found by Hüfner's method, 13·6 must be added to obtain the total nitrogen; and this method of calculating the total nitrogen gives very good practical results.

W. D. H.

Cystin in Normal Urine. By E. GOLDMANN and E. BAUMANN (*Zeit. physiol. Chem.*, 12, 254—261).—Stadthagen (Abstr., 1885, 830) has stated that normal urine contains no cystin, or only minimal quantities of that substance. In 12 experiments, the average amount of sulphur from cystin or allied substances was only 0·0003 gram per litre of urine.

It was thought necessary to repeat these observations, because investigations on the properties of pure cystin showed that Stadthagen's method was not calculated to yield accurate results.

If a few drops of benzoic chloride is added to a solution of pure cystin in sodium hydroxide, a voluminous precipitate of shining plates of the sodium salt of benzoylcystin, $C_6H_{10}N_2S_2O_4Bz_2$, is produced. This salt is soluble in hot, less soluble in cold water, and quite insoluble when excess of sodium hydroxide is present. By adding acid to this, benzoylcystin itself is obtained. It is a strong acid, insoluble in water, slightly soluble in pure ether, more so in a mixture of alcohol and ether, and still more so in alcohol. It crystallises in slender needles, melts at 156—158°, and is decomposed into benzoic acid and cystin by boiling with strong acids. By boiling with alkalis, it yields up its sulphur like cystin.

The circumstance that this compound is easily separated from watery fluids by means of ether, renders it easy to obtain cystin from the urine when it is present there. In some preliminary experiments known weights of benzoylcystin were mixed with urine, extracted therefrom by ether; the ethereal solution was evaporated to dryness, the residue taken up with sodium hydroxide, and the sulphur weighed as lead sulphide. The lead sulphide obtained, however, only corresponded to about two-thirds of the cystin used. On treating normal urine in this way, a precipitate of lead sulphide was always obtained, and the amount of sulphur was always greater than in Stadthagen's experiments, but as the cystin is not all decomposed, no exact quantitative statements can be made. The statement commonly made that cystin gives up its sulphur easily and completely on heating with alkalis is incorrect; after many hours' boiling, the cystin still retains a large percentage of sulphur, and this percentage is still greater in the presence of the other constituents of urine. It can, therefore, be said that cystin or a substance like cystin always occurs in urine, but no accurate quantitative statement can be made on the subject. The quantity was increased in dogs by poisoning with phosphorus. Perhaps different isomerides of cystin exist, which differ in the readiness with which they give up their sulphur. W. D. H.

Spontaneous Decomposition of Bilirubin. By E. Salkowski (*Zeit. physiol. Chem.*, **12**, 227).—In two cases of strongly icteric urine it was noticed that after the occurrence of the ammoniacal fermentation, Gmelin's and Huppert's colour reactions were no longer given. Methods of extraction and precipitation, moreover, yielded no unchanged biliary pigment; dark, amorphous masses only were obtained. This decomposition of bilirubin without the production of any characteristic products, is probably the result of the activity of bacteria, and may probably explain other cases of jaundice in which the urine, though darkly coloured, gave no evidence of bile pigment.

W. D. H.

Poisonous Properties of Dinitrocresol. By T. Weyl (*Ber.*, **21**, 512; compare this vol., p. 184).—Doses of 0·054 gram per kilo. body-weight, suspended in a little water or milk, introduced into the stomachs of dogs (of 5 to 7 kilos.), caused in a few minutes great difficulty in breathing, and convulsions, during which the animals die. Doses of 0·02 gram per kilo. body-weight, dissolved in aqueous alcohol, and applied subcutaneously to moderate-sized dogs, brought on the same symptoms and death in 1 to 1½ hours. Some animals recovered after 3 to 4 hours. N. H. M.

Chemistry of Vegetable Physiology and Agriculture.

Nitrification of Ammonia and its Salts. By H. PLATH (*Bied. Centr.*, 1888, 6—8).—Frank was led to the conclusion that, although certain species of bacteria may be able to help nitrification in the soil, yet in general the action is produced without the intervention of organisms; he isolated various forms of fungi from the soil, and found that they possessed no power of nitrifying ammonia, also that sterilised soil nitrified ammonium chloride about as quickly as the original soil, and he concluded from some experiments that the calcium carbonate of the soil in presence of water and air produces a slow combination of the nitrogen to nitrous and nitric acids. Dumas (1846) found that by passing moist air and ammonia at about 100°, over chalk for some days, a noticeable quantity of potassium nitrate is formed. Later communications state that this happens also at ordinary temperatures. Millon (1860) asserted that humus had a direct action in nitrifying ammonia.

The author's work aimed at a repetition of that of the above experimenters, and he came to the conclusion that when the action of organisms is eliminated by sterilising soil, neither its individual constituents singly, nor the soil as a whole, can nitrify ammonia, and that, further, the nitrifying power must be due to micro-organisms, and, lastly, that the power of oxidising atmospheric nitrogen cannot be ascribed to calcium carbonate. Frank has since protested against Plath's conclusions, objecting that some important experiments of his were not repeated, and that in order to prove that organisms are the nitrifying agents, Plath has yet to show that the heat employed in sterilising produced no change in the soil other than the death of the organisms. H. H. R.

Aspidium Felix, Mas. L. By G. DACCOMO (*Chem. Centr.*, 1887, 1357—1358; from *Ann. Chim. Farm.*, **87**, 69—90).—If the ether extract residue of the rootstock of aspidium (male fern) is treated with 2 vols. of 95 per cent. alcohol and 1 vol. of ether, a brown residue is left which is partially soluble in 1 per cent. aqueous potash. The soluble portion is the filicin or filicic acid of Trommsdorf; the insoluble part separates from an alcoholic solution as a white, floccular, waxy substance, $(C_{13}H_{26}O)_n$, melting at 80°, it is insoluble in water, sparingly soluble in ether and cold alcohol, but soluble in hot alcohol; it is not decomposed by boiling alcoholic potash, and gives no coloration with sulphuric acid and chloroform.

The residue obtained by evaporating the alcohol-ether solution of the original extract, when extracted with water, furnishes glucose and tannin, and with 95 per cent. alcohol a black resin which is almost completely soluble in 2 per cent. aqueous potash. The residue of the extract, insoluble both in water and alcohol, is a green oil difficult to saponify.

The blood-red alkaline solution when agitated with ether parts with some of the red colouring matter (felix red). The residue of this ether extract when distilled with steam furnishes the essential oil of felix; this essential oil appears not to pre-exist in the plant. The residue from this distillation, when extracted with ether, gives, when the ether is evaporated, a red liquid and a precipitate, which, after crystallising from hot alcohol, forms plates melting at 136·5°, having the composition $C_{20}H_{34}O$. This compound has received the name of *aspidol*. It is insoluble in alkalis, easily soluble in ether, benzene, chloroform, light petroleum, and hot alcohol. It is optically active in a 3 per cent. chloroform solution $[\alpha]_D = -24·08$. The filtrate from this precipitate of aspidol was fractionated into three parts. The first fraction, 130—190°, was a yellow oil with a strong odour and acid reaction, which did not reduce silver nitrate. The second fraction, 220—290°, was a beautiful green oil, which gradually became brown; it has the empirical formula $(C_{27}H_{46}O_2)_n$. The third fraction above 300° (at 200 mm. pressure) corresponds with the formula $(C_{34}H_{58}O_2)_n$.

By precipitating the alkaline solution extracted with ether with sulphuric acid, two resins were obtained: 1st, a brick-red solid melting at 85—93°; 2nd, a more abundant and almost black, plastic mass. The filtrate contains butyric acid. J. P. L.

Ensilage Processes. By A. CSERHÁTI (*Bied. Centr.*, 1888, 39—43).—The value of an ensilage process is determined chiefly by the loss of substance, and by the quantity and nature of the acids produced; the two first items should be as small as possible. The author experimented with various fodders ensiled in glass cylinders or in boxes sunk in the ground. On comparing the merits of fresh fodder with wilted fodder for making silage, he found that the temperature rose slightly higher, and that the loss of substance was greater in the case of the wilted fodder. On comparing the effect of stamping the fodder well down in the silo with only stamping it down round the edges, he found that the temperature rose considerably higher in the latter case. Fry's method of allowing the material to heat and rise to 50° in order to stop the development of micro-organisms, and so to diminish the amount of acid formed is most expensive in loss of material. To see whether such a high temperature was necessary, the author tried stamping the fodders well down, and keeping the temperature under 30° as far as possible. He found that although the amount of acid in the silage was higher than that given by Fry, yet it was in itself very small. He concludes that by proper precautions, namely: having perpendicular walls for the silo; using fresh fodder; thorough stamping; having a level covering, and heavy weighting, the amount of acid can be kept down without incurring the loss that the employment of Fry's method involves.

H. H. R.

Ensilage in the Open Air. By M. BARTH (*Bied. Centr.*, 1888, 64). —A description of the way a stack of silage was made, and of the composition of the resulting silage. H. H. R.

Exhaustion of Virgin Soils in Australasia. By R. W. E. MACIVOR (*Chem. News*, 57, 25—26).—The exhaustion of the virgin soils of Australasia is in great part due to the bad system of cultivation giving rise to waste of nitrogen. To grow wheat continuously, the ground is ploughed year after year to a depth of 2½ to 3 inches, thus giving a very shallow surface soil, whilst the continual passage of the shoe of the plough converts the subsoil into a firm compact bed almost impenetrable by the roots of wheat. The surface soil soon becomes dry, and oxidises readily with loss of humus and nitrogen. Another source of loss is the burning the straw. The deficiency of nitrogen is least observed in heavy soils derived from rocks of volcanic origin, then follow those soils traceable to silurian and primitive rocks, whilst light friable soils when in dry and exposed districts are the poorest soils and the greatest sufferers. Soils in New Zealand, Tasmania, and the cooler parts of Australia, contain more nitrogen than soils of the same formation in drier and hotter localities. Dressings of non-nitrogenous manures proved quite useless, and even nitrogenous manures yielded an increased crop without profit. An occasional bare fallow restores matters for a time, but ultimately even that does no good. The introduction of a leguminous crop from time to time has proved beneficial. D. A. L.

Maintenance and Increase of the Amount of Combined Nitrogen on the Farm. By J. KÖNIG (*Bied. Centr.*, 1888, 16—31). —The first part of this article treats of the natural sources of nitrogen to plants, and discusses the work of previous experimenters bearing on the question; then Hellriegel's investigations are described. He found that the Graminaceæ are dependent for their nitrogen on the combined nitrogen of the soil, and that most probably they only avail themselves of it when it has been transformed into nitrates. In the case of the Papilionaceæ it is quite different. When peas were grown in a soil containing no nitrogen, they first used that which was stored in the seed; when this had all been employed, there was for a time an evident halt in their growth which, however, was only temporary, and they eventually succeeded in supplying themselves with nitrogen from some other source. Their subsequent development varied much in different experiments, although the conditions of growth were the same. To discover whether these variations could be due to the combined nitrogen of the air, one set of plants were grown in ordinary air and another set in air freed from ammonia and nitric acid; the results showed that this was not the cause of the variation, and led to the conclusion that the free nitrogen of the air must somehow become available to the peas. An examination of the roots showed that at the period when growth was temporarily arrested the so-called leguminous nodules were absent or only in an incipient state, whilst those plants which were growing properly possessed nodules, and that the older and larger the nodules, the better was the development of the plant. These nodules are full of bacteria, and a series of experiments was made, in which to peas growing in soil containing no combined nitrogen there was added, in some cases, an aqueous extract of fertile soil, in others the same extract after sterilisation, and in others again no such addition was made. It was found that the nodules and the thriving of the plant could be produced or prevented at will by the addition or exclusion of micro-organisms.

The growth of lupines on soil containing no combined nitrogen was also investigated, and it was found that they would never attain a satisfactory development when exposed to the same opportunities of receiving germs from the air that enabled some of the peas to thrive; hence it was inferred that the bacteria which occur in the root nodules of lupines are different and less widely diffused than those occurring in peas. This view was supported by the facts that the nodules are different in shape and position on the two plants and contain micro-organisms of obviously different appearance, and also that lupines do not thrive on heavy or rich soil. It was put to the test by growing lupines in sand containing no combined nitrogen, and treating one part of them with an aqueous extract of the soil of a lupine field, a second part with an extract of a clay-marl containing humus and not growing lupines, and leaving a third part without any such addition. All three parts exhibited a period of arrested growth, then the first part started growing and showed nodules like ordinary lupines, the second part showed traces only, and the third part showed no traces of nodules at all.

Of other plants examined, Serradilla (*Ornithopus sativus*) behaved like lupines, whilst vetches and beans (*Vicia faba*) like peas developed best when treated with extract of rich soil; red clover gave no decided result. It thus appears that the Papilionaceæ are not dependent on the soil alone for their nitrogen, but that they can make use of the free nitrogen of the air, and that the root nodules and the micro-organisms in them are in close and active relationship to the nourishment and especially to the assimilation of nitrogen by these plants. It must not, however, be inferred that the combined nitrogen of the soil is of no importance to them, for Hellriegel found in some experiments that they could make use of nitrates; although it seems questionable whether nitrates could produce a normal development if micro-organisms were absolutely excluded.

Notwithstanding these researches, it is stated in the article to be still an open question whether the root nodules can change free nitrogen into nitrogenous compounds, although the growth of Papilionaceæ is strongly recommended as a means of increasing the combined nitrogen on the farm. To this same end, irrigation by brook and river water is recommended, as a great part of the combined nitrogen dissolved in the water is retained in the form of plant substance.

The second section treats of the ways in which combined nitrogen may be set free and lost, namely: (1) during germination; (2) in the processes that go on in the animal body (both of which ways have been disputed); (3) during the putrefaction of nitrogenous substances; (4) during the decomposition of organic manures in the soil, especially when it is too strongly aërated by drainage, and nitrification consequently goes on too actively. This section also gives numerous directions for avoiding loss of combined nitrogen in the keeping and employment of manures. H. H. R.

Manuring Experiments on Oats. By K. Müller (*Bied. Centr.*, 1888, 103—107).—The experiments seem to show that an oat crop following wheat after sugar-beet is grateful for phosphatic and nitrogenous manuring, even when the roots have been excessively manured with phosphates. Chili saltpetre alone produced an increase in grain and straw, the largest increase of grain being caused by the saltpetre in combination with precipitated phosphate, and the lowest by the saltpetre and superphosphate, the greatest increase in straw was produced by an inverted order of phosphates, basic slag holding a middle place in both cases. Placing the expense of manures against the increase in crop, it appeared that saltpetre was the most renumerative, whilst superphosphate and saltpetre together were applied at a loss. E. W. P.

Increase in Yield of Crops by Nitrogenous Manures. By P. Wagner (*Bied. Centr.*, 1888, 78—96).—The author draws his conclusions from experiments made by himself, by Märcker, and others; it does not seem that the addition of saltpetre to leguminous crops is of any value, as the increase in yield is so very little, in fact, in some cases there appears to be a decrease in the yield, as the quantity of saltpetre increases. On the other hand, this manure is of value to straws and roots. Employing E. Lierke's tables, Wagner shows how varied is the money value of saltpetre with the different crops in cultivation, and the many circumstances which militate against the complete and successful action of nitrates; to obtain the best result all the necessary plant food must be present in full quantities, to say nothing of want of rain and warmth. The variations in the yield of grain or straw are fully entered on, as well as the causes of such variations. Ammoniacal manures are frequently unsatisfactory, although theoretically the quantity of nitrogen added may exceed that which would be contained in a dressing of nitrate; this probably arises from the fact that the conversion of the ammonia is so slow that the plants do not obtain a sufficiency of nitrate within the requisite time, consequently being "hungered" they are unable to make full use of the other plant foods; it is on this account that ammoniacal manures should be applied to the soil some time before the seed is sown, so that there may be a sufficiency of nitrates present to allow of full, rapid, and unhindered growth. E. W. P.

Manurial Action of the Free Lime in Basic Slag. By E. Jensch (*Bied. Centr.*, 1888, 12—16).—The activity of basic slag on soils poor in lime has often led to the free lime in the slag rather than the phosphate being regarded as the active agent. To examine this question six sets of experiments were made with oats grown in pots. A loamy soil was chosen, and it was used both in its natural state and also after having been treated with dilute hydrochloric acid for some time and then washed. The manures employed were (1) basic slag meal in its original state; (2) basic slag meal which had been treated with sugar solution to remove free lime; (3) lime, and (4) potassium nitrate which was added uniformly to all the pots. The results of the experiments showed that the phosphate in slag from which the free lime had been removed gave nearly as good a yield as in that which still contained free lime, and that although a certain amount of benefit cannot be denied to the free lime, still the increased yield was chiefly due to the phosphate. H. H. R.

Analytical Chemistry.

Filtration Apparatus. By F. ALLIHN (*Zeit. anal. Chem.*, **26**, 721).—The stem of the funnel has a bulbous expansion, which is ground into the neck of a thick-walled flask. This has a side-tube for connection with the air-pump. M. J. S.

Improved Form of Nitrometer. By G. LUNGE (*Ber.*, **21**, 376—377).—The improvement consists in substituting Friedrich's patent diagonally bored stopcock for the ordinary three-way stopcock of the nitrometer. W. P. W.

Estimation of Iodine. By N. MCCULLOCH (*Chem. News*, **57**, 45—48).—Manganic oxide suffers slight reduction in presence of iodine (compare Abstr., 1887, 1141), and therefore titration of iodine by means of alkaline permanganate is inaccurate, and cannot be employed for the determination of iodine in presence of a chloride or bromide, although the latter are not oxidised under the conditions. Hydrogen peroxide is also unsuitable for the purpose. The author therefore proposes to eliminate the chloride and bromide by a process described in the paper in which the mixture containing the chloride, bromide, and iodide is heated with permanganate and strong sulphuric acid, the first two elements are driven off as hydrogen chloride and bromide respectively, whilst the whole of the iodine is oxidised to iodic acid. The solution is diluted, filtered, reduced by means of sulphurous acid, and the iodine determined either by precipitation as silver iodide, or by titration with permanganate in presence of free sulphuric acid and hydrocyanic acid; the latter forms colourless cyanogen iodide with the iodine set free by the sulphuric acid, which would otherwise mask the end reaction. This method of titration is free from the error of reduction of manganic oxide referred to above, and also from the inconvenience of the precipitated manganic oxide accompanying the use of alkaline permanganate. It cannot, however, be used in presence of hydrobromic acid or of the reducing salts of copper, iron, &c.

D. A. L.

Indirect Determination of Fluorine. By S. Bein (*Zeit. anal. Chem.*, **26**, 733—736; from *Rep. anal. Chem.*, **6**, 169).—The fluorine is expelled as silicon fluoride by heating the substance with powdered quartz and sulphuric acid, and is driven over by a stream of dried air into water. The fluoride and the quartz sand (12 parts) must be very finely ground and intimately mixed. The mixture is placed in a dry flask having a cork through which pass a tube for the admission of dried air, the tube of a separator bulb containing sulphuric acid, and a tube for conveying the gases into water. The last has the outer limb widened. For 1 gram of calcium fluoride, 50 c.c. of sulphuric acid is added and the flask is heated for three hours at 165° with occasional shaking. A further quantity of acid is then added, and the heating and shaking are continued as long as the gas bubbles produce any precipitate. After collecting and washing the silica by suction, it may be at once ignited without previous drying. One part corresponds with 5·494 parts of fluorine.
M. J. S.

Estimation of Selenium. By H. N. Warren (*Chem. News*, **57**, 16).—See p. 435.

Estimation of Nitrites. By A. Vivier (*Compt. rend.*, **106**, 138—140).—The apparatus is similar to that used in the estimation of nitrites and nitrates by Schloesing's method. The air is first expelled by boiling a small quantity of water in the flask, and the solution of the nitrite is introduced, followed by a solution of carbamide, and finally by dilute sulphuric acid. A current of carbonic anhydride is passed through the apparatus during the whole operation. The mixture is gradually heated and finally is boiled for several minutes, the gas which is evolved being passed through potash solution to absorb carbonic anhydride, whilst the nitrogen is collected and measured. Care must be taken to expel the nitrogen from the flask at the close of the operation by the current of carbonic anhydride. The volume of nitrogen obtained is double that existing as a nitrite.
C. H. B.

Free Acid in Superphosphates. By W. W. Mellon (*J. Soc. Chem. Ind.*, **6**, 803—805).—The average amount of free acid found in 485 samples of manures of various kinds examined was equal to 8·54 per cent. H_3PO_4; the highest being 16·36 per cent. and the lowest 2·36 per cent. The results of some experiments are given which show that the amount of free acid and soluble phosphate is affected by the method of extraction adopted, and by the strength of the acid used to decompose the phosphate. The free acid always present in manures seems to consist mainly of phosphoric acid with smaller amounts of hydrofluosilicic acid, hydrofluoric acid and (occasionally) sulphuric acid. The latter was found only in damp samples containing a large amount of free acid. The presence of free hydrofluosilicic and hydrofluoric acids in manures seems to have escaped observation; in the ordinary course of manure analysis, in which the moisture is determined by heating the sample for several hours in the water-bath, they are volatilised and reported as moisture. The average amount of volatile free acids found in 14 samples was equal to 2·30 per cent., H_3PO_4, the highest being 3·96 per cent. and the lowest 0·96 per cent. They were estimated by evaporating a solution of the manure to dryness in a platinum dish, the residue was dissolved in water to which a known amount of standard acid had been added, and the solution titrated with standard alkali. The loss of free acid on evaporation equals the total volatile acidity calculated as H_3PO_4. The amount of free hydrofluosilicic acid found in the 14 samples tested, comprised about two-thirds of the total volatile acidity. The estimation was made by evaporating to dryness a solution of the manure to which some potassium sulphate, neutral to methyl-orange, had been added, the residue being dissolved in standard acid and titrated as before. The increase in the amount of free acid as H_3PO_4, after evaporation with potassium sulphate, as compared with the amount found on evaporating the solution *per se*, is equivalent to the free hydrofluosilicic acid present. D. B.

Determination of Arsenic as Pentasulphide. By L. W. McCay (*Amer. Chem. J.*, 9, 174—180).—The tedious precipitation of arsenic pentasulphide according to the directions of Bunsen may be replaced by a very simple, rapid and efficacious method, namely:—the solution containing arsenic acid equivalent to about one to three tenths of a gram of the pentasulphide, is placed in a bottle of 200 c.c. capacity provided with a well-ground stopper; the bottle having been almost filled with freshly boiled water, and the contents saturated with hydrogen sulphide, it is closed, the stopper tied down, and the whole placed in a water-bath for one hour. The precipitate is most easily removed from the bottle, and, the air having been excluded, contains no free sulphur, and does not require to be washed with alcohol and carbon bisulphide. When arsenious acid is treated with hydrogen sulphide in presence of air, but otherwise as above described, it is converted into the trisulphide, no pentasulphide being formed. H. B.

Quantitative Analysis by Electrolysis. By A. Classen (*Ber.*, 21, 359—369).—A simple form of rheostat is described which affords the means of carrying on simultaneously with one battery eight determinations of different metals requiring different strengths of current, and a number of very concordant results obtained by its use are detailed. A new form of voltameter is also described, consisting of a vertical, stoppered, graduated tube expanded at its lower portion into a cylindrical chamber containing the platinum electrodes, which is connected to a second vertical pressure tube by means of india-rubber tubing. This arrangement renders it possible for the gas in the voltameter to be measured at the atmospheric pressure. A description is also given of a stand for the support of the platinum dish forming the cathode and of the anode, whose chief point of novelty consists in the substitution of glass for brass for the material of the rod which supports the arms.

Estimation of Copper in the Presence of Arsenic.—In the presence of more than 0·2 per cent. of arsenic, it has been found impossible in practice to employ the electrolytic method for the deposition of copper with satisfactory results without previously removing the arsenic by precipitation. This, however, is now unnecessary if the ore has not been roasted, since the whole of the arsenic may be volatilised as arsenic bromide by evaporating it several times on a water-bath with a solution of bromine in hydrochloric acid; the residual bromine compound of copper is then decomposed by ignition with sulphuric acid, dissolved in water, treated with the requisite quantity of nitric acid, and afterwards electrolysed.

Separation of Copper from Lead.—A platinum dish and plate are employed as anode and cathode respectively. To 120 c.c. of the solution containing the two metals, 30 to 40 c.c. of nitric acid (sp. gr. = 1·2) is added, and the resulting solution is electrolysed at first with a current giving in the voltameter 0·1 c.c. of gas per minute, and afterwards, when the lead peroxide has formed a distinct layer on the dish, with a current giving 3 c.c. of gas per minute. At the end of the operation, about 10 c.c. of water is added, the current continued for an hour longer, and then, without interrupting it, the contents of the dish are washed out with water. Treatment with alcohol removes the water adhering to the dish and plate, and these are then dried at 110° until the weight is constant. The lead peroxide adheres firmly to the dish even in quantities of more than 0·2 gram.

W. P. W.

Analysis of Lead Slags. By M. W. ILES (*Chem. News*, **57**, 18—19).—See this vol., p. 418.

Estimation of Thallium. By G. NEUMANN (*Ber.*, **21**, 356—359).—The volume of hydrogen evolved when electrolytically deposited thallium is treated with an acid may be employed as a means of estimating the metal. The thallium salt, together with about 5 grams of ammonium oxalate, is placed in a flask of about 100 c.c. capacity provided with two platinum electrodes 9 sq. cm. in area, and the electrolysis of the slightly warm solution is effected by a current of E.M.F. = 0·1 volt. (?) About 0·6—0·8 gram of the metal, which adheres firmly to the cathode, can be deposited in seven hours, and the end of the reaction is ascertained by testing with ammonium sulphide. Owing to the formation of ammonium carbonate during the electrolysis, it is necessary to remove the liquid in the flask before treating the deposited thallium with an acid; this is effected by drawing a current of water through the apparatus by means of siphons arranged in such a way that contact of the metal with the air is excluded. The electric current is maintained during the washing, and afterwards the contents of the flask are heated to remove occluded gas from the electrodes. The flask is then attached to the author's "hydrometer" (Abstr., 1887, 1140), and the gas evolved on treatment with an acid is measured. The method is applicable to the estimation of the metal in its carbonates, nitrates, chlorides, and sulphates, and the error does not exceed 0·2 per cent.

W. P. W.

Analysis of Iron and Iron Ore. By A. TAMM (*Chem. Centr.*, 1887, 1362; from *Stahl u. Eisen*, **7**, 627—633).—To avoid error in the determination of phosphorus, the author evaporates the nitric acid solution, which might contain phosphorous acid, to dryness and heats to 200°.

The use of hydrofluoric acid, as recommended by Wood to keep the silica in solution, he regards as superfluous and dangerous, inasmuch as phosphoric acid might be dissolved from the glass. In the case of iron containing manganese, the iron with the phosphoric acid must first be separated with manganese acetate; in the case of iron containing much chromium, complete decomposition only occurs if the quantity of chromium is lessened by fusing together with it iron containing a small but known quantity of phosphorus.

The estimation of sulphur presents difficulties both on account of the possibility of incomplete oxidation of the sulphur and the incomplete precipitation of barium sulphate in presence of ferric chloride. To avoid the latter error, the silica is rendered insoluble by evaporating to dryness, the residue taken up with hydrochloric acid, the solution filtered and again evaporated to dryness, after the addition of barium chloride, and again taken up with hydrochloric acid.

To determine graphite, the iron is dissolved in nitric acid of sp. gr. 1·20, which leaves only graphite undissolved. J. P. L.

Modified Method of Estimating Iron Volumetrically by means of Potassium Dichromate. By H. Bya (*Dingl. polyt. J.*, **266**, 606).—In order to reduce the iron to the ferrous state the author, for the sake of rapidity, recommends the use of stannous chloride instead of nascent hydrogen, the excess of reducing agent being removed by the addition of mercuric chloride to the solution previous to the titration with potassium dichromate. D. B.

Determination of Carbon in Steel. By B. Blount (*Chem. News*, **57**, 27—28).—The method of determining carbon in steel by dissolving in dilute acid, passing the gases evolved over red-hot copper oxide, and weighing the carbonic anhydride, yields low and irregular results; this the author attributes to the formation of less volatile hydrocarbons, which in the first instance escape being carried over the copper oxide by the gaseous products, and in the second case are filtered off from the solid carbonaceous residue and consequently escape the subsequent chromic acid oxidation; the irregularity being due to slight variations in temperature and in the rate of dissolution. The author suggests as a remedy boiling off most of the water in the flask after solution is complete, and allowing the steam carrying with it the less volatile hydrocarbons to pass over the copper oxide without previous condensation. When methods involving the dissolution of steel in copper sulphate are resorted to, the following plan will expedite the dissolving, and avoid the deposition of copper with the carbon; the steel is placed on a platinum plate forming the positive pole, having a copper negative pole suspended in the liquid, and a current slightly below the strength required for the removal of the copper is passed through; this precaution being taken to prevent oxidation of the carbon. D. A. L.

Analysis of Nickel. By G. LANGBEIN (*Zeit. anal. Chem.*, 26, 731—732; from *Rep. anal. Chem.*, 6, 423).—In the electrolytic deposition of nickel from a solution containing manganese, part of the latter may be deposited in the metallic form in company with the nickel. The manganese should therefore be first removed. The nitric acid solution of the alloy (2 grams) is mixed with sulphuric acid and electrolysed for removal of copper. It is then evaporated with more sulphuric acid until fumes of that acid escape. After dilution, excess of ammonia is added and the mixture is kept warm for five or six hours. Since ammonium chloride is absent, the manganese precipitates with the iron, but a little nickel accompanies the precipitate and must be separated by dissolving in warm sulphuric acid and precipitating twice more in the same way. An aliquot part of the solution is then mixed with ammonium chloride and ammonia and electrolysed. Any magnesium present may be determined in the liquid decanted from the nickel. M. J. S.

Quantitative Separation of Chromium and Uranium. By J. FORMÁNEK (*Chem. Centr.*, 1887, 1407—1408; from *Listy. chem.*, 11, 217—220).—Separation of chromium and uranium by precipitating the chromium as mercurous chromate in the warm and weighing the chromium as Cr_2O_3 after ignition is not satisfactory, as some uranium is liable to be carried down with the precipitate; on the other hand, some of the mercurous chromate remains in solution if too much acid is present. The mercurous nitrate solution, too, is liable to undergo alteration from oxidation, oxides of nitrogen being formed which reduce the chromate and cause loss. Observing all due precautions, the results are still 1 per cent. too low. If a solution containing uranium and an alkaline chromate is precipitated with soda, the precipitate of uranium should be washed with weak soda, dissolved in hydrochloric acid, and reprecipitated with ammonium sulphide, as recommended by Zimmermann. Ammonia is likely to precipitate some of the alkali as uranate. Ditte's process is not recommended, for not only does uranium remain in solution but the separation of the precipitate of the combined oxides ($Cr_2O_3 + UO_2$), after ignition in hydrogen, cannot be completely effected by means of nitric acid. J. P. L.

Separation of Tin Oxide from Tungstic Acid. By E. DONATH and F. MÜLLNER (*Monatsh. Chem.*, 8, 647—649).—The ignited and weighed mixture of tin oxide and tungstic acid is rubbed in an agate mortar with twice its volume of zinc-dust or zinc-filings and turned into a small porcelain crucible. The covered crucible is strongly ignited for 15 minutes, the contents emptied into a beaker, and treated with hydrochloric acid (diluted with two parts of water). It is then boiled until the evolution of hydrogen ceases, and treated with powdered potassium chlorate until the blue tungstic oxide is oxidised to tungstic acid. Water ($1\frac{1}{2}$ vols.) is added to the solution, and it is filtered after 24 hours. The tungstic acid is washed with water containing nitric acid and then with a hot dilute solution of ammonium nitrate; finally it is dried, ignited, and weighed.

The amount of tin oxide can be calculated or may be determined by precipitating the tin as sulphide and weighing as oxide. In this case, zinc-dust must not be used, as it contains cadmium, which would affect the results. N. H. M.

Quantitative Separation of Titanium from Iron. By A. CLASSEN (*Ber.*, 21, 372—375).—The behaviour of titanium trioxide (this vol., p. 424) with alkalis affords a convenient and accurate method of qualitatively and quantitatively determining titanium in the presence of iron, and of all those metals which are precipitated by alkalis; for example, 0·02 per cent. of titanium dioxide in an iron solution can readily be detected by its means. To estimate the quantity of titanium in iron, the usual quantity of material dissolved in hydrochloric acid is freed from excess of acid by evaporation, then treated with 50 c.c. of hydrogen peroxide, and 25 c.c. of aqueous potash, and diluted to a known volume. A wash-water is employed containing 100 c.c. of hydrogen peroxide in the litre and some aqueous potash (sp. gr. = 1·3), and the precipitate is washed by decantation until the washings are no longer coloured yellow on treatment with hydrochloric acid. The precipitated iron is dissolved in the smallest possible quantity of dilute sulphuric acid, converted into the double salt with ammonium oxalate, and estimated by electrolysis; any titanium dioxide or aluminium hydroxide associated with the iron remains in suspension in the liquid. To decompose the hydrogen dioxide, the filtrate from the precipitated iron is heated in a water-bath until the evolution of gas ceases. A portion of the titanium is in this way precipitated as trioxide mixed with some dioxide, and the remainder is precipitated as dioxide by heating the liquid rendered acid with hydrochloric or nitric acid until it is decolorised; ammonia is then added in the smallest possible excess, and the precipitated oxide filtered off, washed, ignited, and weighed. Should the iron or hydrogen peroxide contain silica, it is necessary to moisten the ignited oxide with dilute sulphuric acid, and treat with hydrofluoric acid; the residue is then again ignited. Any alumina can be separated from the precipitate by the ordinary methods (compare Gooch, Abstr., 1885, 1265). W. P. W.

The Air of Sewers. By T. CARNELLEY and J. S. HALDANE (*Proc. Roy. Soc.*, 42, 394—396, and 501—522).—The authors have examined the air of sewers under various conditions. They find that the amount of carbonic anhydride is about twice as great, the amount of organic matter about three times as great as that of the outside air, whilst the number of micro-organisms is considerably less than in ordinary air. These micro-organisms are considered to be derived from the outside, and not from the sewage, (1) from the fact that the ratio between bacteria and moulds is the same as that in the outside air; (2) that the better the ventilation of the sewer, the greater the number of micro-organisms; and (3) because the number of micro-organisms was found to decrease the greater the journey of the air through the sewers, provided always that splashing did not take place. This retention of micro-organisms by the wet sides of the sewers was proved by means of an experimental sewer. Where splashing occurs, however, a sudden rise in the number of bacteria is found to take place, the bacteria being derived from the sewage itself. The organic matter of the sewer air was almost entirely gaseous, and did not contain anything of the nature of ptomaïnes.

H. K. T.

Determination of Carbonic Acid in Mineral Waters. By W. Borchers (*Zeit. anal. Chem.*, **26**, 720).—In *J. pr. Chem.*, **17**, 353, the author described an apparatus and method for determining successively in one and the same portion of a mineral water the carbonic acid existing in the three forms of metallic carbonate, metallic hydrogen carbonate, and free carbonic acid. The last two are expelled by boiling and the transmission of purified air, the first by adding an acid. It is now recommended to convert the alkaline hydrogen carbonates by the addition of barium chloride into barium hydrogen carbonate, which gives up its second molecule of carbonic acid at a much lower temperature. M. J. S.

Determination of Phosphoric Acid in Contaminated Waters. By T. L. Phipson (*Chem. News*, **56**, 251).—This method can be employed for the detection and determination of very minute quantities of phosphoric acid. About a pint of the water is treated successively with a very small quantity of potash alum in solution, a drop or two of ammonia, and acetic acid until distinctly acid. The precipitate of aluminium phosphate thus formed is dissolved in nitric acid, and the phosphoric acid determined in the usual way.

D. A. L.

Experiments on Heisch's Method for Detecting Sewage Contamination in Water. By F. E. Lott (*J. Soc. Chem. Ind.*, **6**, 495—499).—The author's experiments completely confirm the observations made by Frankland many years ago, but, being applied to potable waters, they are of some interest as indicating how far Heisch's test may be looked to for information as regards the purity of such waters. On this head, the author's experiments lead him to conclude that—(1.) Any water undergoing butyric fermentation when simply treated with cane-sugar and kept at a temperature of about 26° may at once be condemned as unfit for domestic use. (2.) The single fact of a water not undergoing butyric fermentation is no proof of its purity. (3.) A water which remains clear under this treatment would be less likely to be contaminated by sewage than one which became milky. (4.) The butyric ferment is not perceptibly influenced by the presence of abnormal amounts of chlorine, free ammonia, albuminoïd ammonia, sulphates, and nitrates in a water, but is a very accurate indicator of the presence of phosphoric acid.

D. B.

Determination of Ammonia in Arable Soils. By W. Knop (*Zeit. anal. Chem.*, **26**, 690—699).—A reply to Baumann's criticisms (Abstr., 1887, 82; see also Knop, *ibid.*, 297). The contraction observed when a soil rich in humus is shaken with potash and air is undoubtedly due in part to absorption of oxygen, but not entirely so, since contraction occurs when hydrogen is substituted for air, and appears to result from the humus occupying less space after than before solution. It may be reduced to an insignificant amount by the use of a large quantity of saturated borax solution. A certain amount of contraction is, however, observed when ferruginous clays free from humus (or freed from organic matter by long boiling with chromic acid) are shaken with strong soda. It is not exhibited by pure kaolin, and possibly may not be by soils containing little iron. In any case, it is complete in five minutes, whereas the contraction due to humus is proportional to the time of shaking. The very large contractions observed by Baumann seem to have resulted from the use of too small a quantity of borax solution, thus both enclosing far too much air in the decomposition flask, and at the same time failing to dilute the hypobromite solution sufficiently. Knop fills the flask to within 40 to 50 c.c., and uses much less hypobromite (10 c.c. to 100 grams) than Baumann seems to have done. To the objection that other nitrogenous substances give up nitrogen when treated with hypobromite, it is replied that from a manurial point of view they may be regarded as equal in value to ammonia, and considering the very small quantity of nitrogenous matter present, the fact that some of these substances do not give up the whole of their nitrogen can only introduce a most insignificant error. M. J. S.

Estimation of Carbon in Arable Soils. By O. K. STACHOVSKY (*J. Russ. Chem. Soc.*, 1887, 125—132).—In 1882, Dokutschaéff's investigation "On Russian 'Black Earth'" was published, in which this author has shown the distribution and boundaries of arable soil and the "black earth" in Russia. Carbon was determined by Wolff's method, namely, oxidation with chromic acid. In 1883, Loges (Abstr., 1883, 247) investigated Danish soils and found that the results obtained by Wolff's method were too low as compared with those obtained by combustion with copper oxide. The same result had been obtained by Peak and Warington at an earlier period (Trans., 1880, 617). The author has investigated whether and how far the said difference refers to the case of the "black earth." He uses for oxidation not chromic mixture (the chromic sulphate formed interfering with complete oxidation—the lower numbers found by Loges may perhaps be due to this cause), but an aqueous solution of chromic anhydride. The carbonic anhydride is absorbed in Classen's apparatus (a vertical condenser and two soda-lime tubes). The results obtained by the author with different samples of "black earth" by the chromic acid method agree completely with those obtained by combustion with copper oxide, but of course the first method requires far less time than the second.

When, however, substances containing humous matter, such as peat, were analysed, much lower results were obtained with chromic acid. The author thinks that the good results obtained with Russian "black earth" are probably due to the presence of large quantities of nitrogenous substances in "black earth," which by oxidation are possibly converted into nitric acid and nitrogen oxides; these being good oxygen carriers assist in completing the oxidation of the carbon.

B. B.

Estimation of Grape-sugar in Urine. By H. WILL (*Arch. Pharm.* [3], **25**, 812—822).—The urine is mixed with an equal volume of one-fifth normal baryta solution, filtered, and to 5 c.c. of the filtrate another 5 c.c. of baryta solution is added, together with 100 c.c. of 90 per cent. alcohol; after agitation, the solution is set aside for two or three hours. The precipitate is collected, washed with 20 c.c. of 90 per cent. alcohol, and thrown, along with the filter, into the precipitating flask, in which 10 c.c. of decinormal sulphuric acid has previously been placed. After warming and shaking, the excess of sulphuric acid is neutralised with standard baryta solution, using as indicator not more than one drop of phenolphthaleïn solution (1 : 100). The barium sulphate is now filtered off, and the filtrate is evaporated to dryness and weighed. The grape-sugar remains as a yellowish mass containing a little baryta, which is obtained as carbonate on ignition. This weighing of the sugar serves as a check on the volumetric estimation by means of the baryta precipitate, as described. The author concludes that:—I. Grape-sugar in aqueous solution can be very accurately estimated by the baryta method, either by titrating the baryta or by weighing the separated sugar. II. When baryta in sufficient excess is present, the aqueous solution of the barium sugar compound is precipitated as $BaO(C_6H_{12}O_6)_2 + BaO$ on the addition of so much alcohol that the whole mixture contains 81 to 86 per cent. of alcohol by volume. III. In the presence of only 68 to 70 per cent. of alcohol, the precipitate has the composition $BaO(C_6H_{12}O_6)_2$. IV. In diabetic urine, the results obtained with Fehling-Soxhlet's titration method agree closely with those yielded by the baryta method. J. T.

Formation of Levulinic Acid, a Reaction for the Detection of Carbohydrates. By C. WEHMER and B. TOLLENS (*Annalen*, **243**, 314—334).—Most of the contents of this article have already been published (Abstr., 1886, 532). The authors find that levulinic acid is not produced in appreciable quantities when normal urine is heated with mineral acids, showing that normal urine does not contain carbohydrates. W. C. W.

Determination of Tartaric Acid. By F. GANTTER (*Zeit. anal. Chem.*, **26**, 714—719).—In carrying out Goldenberg's method (this vol., p. 327), Wiegert (*Zeit. anal. Chem.*, **23**, 359) adopts the following precautions. 1. The excess of potassium carbonate should be as small as possible. 2. Acetic acid must be added in corresponding excess. 3. It must be washed out long enough. 4. The acidified mixture must still contain water when the alcohol is added.

To these the author adds that a larger quantity of substance than was originally prescribed must be used. Of argol, lees, or crude calcium tartrate, 10 grams, of residues, 30 grams should be taken, and in both cases one-half of the solution should be used for precipitation. The one or two minutes which is sufficient for the complete decomposition by acetic acid when working with pure substances, is not long enough with crude materials. The evaporation must be stopped at 20 to

30 c.c., the acetic acid added gradually and well stirred in, and the mixture warmed for 15 minutes on the water-bath. M. J. S.

Determination of Tartaric Acid in Wine Lees and Tartar. II. By A. Bornträger (*Zeit. anal. Chem.*, 26, 699—714).—In the experiments in Part I (Abstr., 1886, 1082), the precipitated potassium hydrogen tartrate was always allowed to deposit during the night. A series of comparisons is now made between the results obtained by stirring continuously for 10 minutes and filtering after half an hour, and those yielded by stirring for five minutes and then leaving during the night. The quantity of potassium hydrogen tartrate used was varied from 1·5 to 4 grams, and both 1·5 and 3 grams of oxalate was tried with each quantity of tartrate. Practically identical results (99·51 to 99·72 per cent.) were obtained in all cases.

Grosjean's precaution to prepare the washing liquid exactly at the temperature of the air and to ascertain its actual saturation with potassium hydrogen tartrate by titration, is found to be needless. It suffices to take a hot solution of the tartrate, cool it to about 4° above the temperature of the air, add 10 per cent. of potassium chloride, stir 10 minutes, leave to stand for half an hour, and filter. Even if its temperature differs a few degrees from that of the air it is of no consequence. It should, however, always be freshly prepared.

The following is a more convenient method than Grosjean's for determining the quantity of oxalate required for decomposing the calcium salts. The roughly weighed substance (7·5 grams of lees or calcium tartrate or 3·75 of tartar) is neutralised, and carbonic anhydride is boiled off. Oxalate is then added in quantities of 1·5 grams at a time, heating for 10 minutes after each addition, and testing a filtered sample (acidified with acetic acid) for oxalic acid. Since the amount ascertained in this way can never be more than 1·5 grams in excess, and since any amount between 1·5 and 3 grams is admissible, the amount so employed is increased by 1·5 grams in the actual analysis. In an artificial mixture made to represent lees, and containing calcium sulphate, an hour's heating with the oxalate was found still to leave some of the sulphate undecomposed. A precipitate of calcium oxalate was therefore obtained during the evaporation of the filtrate, and had to be filtered off.

The paper concludes with a minute description of the author's mode of procedure, which, however, only differs from Grosjean's in so far as it embodies the suggestions of this and the previous communications.

M. J. S.

Qualitative and Quantitative Test for Resin Oils in Mineral Lubricating Oil. By L. Storch (*Chem. Centr.*, 1887, 1419; from *Ber. österi. Ges. chem. Ind.*, 9, 93—95).—If to one or two drops of resin oil, 1 c.c. of acetic anhydride and a drop of concentrated sulphuric acid are added, a violet colour is immediately produced which soon changes to brown.

The presence of fixed oils or mixtures of fats prevents the reaction. If the presence of resin oil is shown in a lubricant, the quantitative estimation is made as follows :—To a quantity of the oil, five times its volume of 96 per cent. alcohol is added, and the mixture shaken. The alcoholic solution, which contains the resin oil with a small admixture of the mineral oil, is poured off and evaporated. The residue is weighed and then treated with 10 times its volume of alcohol; any mineral oil undissolved is separated, and the alcohol again evaporated, and the residue weighed a second time. A correction for the amount of mineral oil left in the second residue can be made from the data furnished by the difference in weight of the two residues, and the amount of alcohol used. J. P. L.

Modified Soxhlet's Apparatus. By J. J. Barlow (*Chem. News*, **57**, 56—57).—In the apparatus described, the substance to be extracted, wrapped in a piece of calico, is suspended from a hook in the flask containing the ether. The flask is fitted with a double-bored cork, carrying two tubes, one short and bent to form a syphon whose longer limb delivers immediately above the substance, the other long and straight; these tubes are enclosed in a wider tube fitting over the cork, and connected with a condenser. The advantages claimed are simplicity, the constant exposure of the substance undergoing extraction to hot ether and hot ether vapour, and the easy recovery of the ether at the close of the extraction.

D. A. L

Determination of Butter in Milk. By H. N. Morse and W. M. Burton (*Amer. Chem. J.*, **9**, 222—231).—The following improvements are suggested for the process described (Abstr., 1887, 752). The mixture of milk and copper sulphate is ground whilst still somewhat moist, and in filling the extraction tube, the mixture is packed somewhat tightly by use of a glass rod. Treatment two or three times with light petroleum (15 c.c. each time) is ample for the extraction of the fat. The light petroleum solutions are heated on the water-bath for 20 minutes with so much potash dissolved in alcohol as will saponify 0·1 gram of butter, and finally the excess of alkali is estimated with hydrochloric acid, using phenolphthaleïn as indicator.

Light petroleum, boiling at 45—60°, is as efficacious as that boiling at 30—45°; it is not necessary to remove the petroleum before saponifying; from the examination of a number of samples, it is shown that practically identical results are obtained by weighing the fat extracted, or by saponifying, or by conducting the whole operation as above, and that the amount of alkali required to saponify a given weight of butter is very constant; the variations noticed by Koettstorfer (0·2215 to 0·2324 gram potassium hydroxide per gram of butter) are due to the fact that when butter is fused and allowed to cool without agitation, a partial separation of the constituents takes place, and the mass is not homogeneous. The authors find that 0·02295 gram of potash is required for 0·1 gram of butter.

H. B.

Determination of the Dry Residue and Fat in Milk and Butter. By F. Gantter (*Zeit. anal. Chem.*, **26**, 677—680).—As a porous material for absorbing the milk to be dried, the author prefers wood-fibre, such as is prepared for the manufacture of paper. It requires to be washed with light petroleum. About 2 grams are placed in a capsule, dried at 105°, and weighed together with a small glass rod. Being very hygroscopic, a cover is necessary. The milk (5 or 6 grams) is poured on the fibre, avoiding as far as possible any wetting of the capsule, and during the evaporation the fibre is stirred occasionally in such a way as to wipe the capsule clean. After one hour, it can be transferred to the drying oven, where 1½ hour is long enough for drying the residue from 6 grams of even a very rich milk. The fibre is then removed from the capsule, wrapped in paper, and extracted in Soxhlet's apparatus with light petroleum. Here two hours' extraction is found to be sufficient. In determining the water in butter, 3 grams of fibre should be used for 5 grams of butter. Owing to the large surface exposed, a constant weight is obtained after 1½ hours' drying. M. J. S.

New Method of Examining Butter. By T. T. P. B. WARREN (*Chem. News*, **56**, 262; compare this vol., p. 199).—Both cotton-seed oil and cocoa-nut oil were found in a sample of oleomargarine, although the latter was free from taste and smell; subsequent experiment showed that by mixing cocoa-nut oil with a certain quantity of cotton-seed oil, its odour and taste are concealed; when, however, these two oils are present in oleomargarine, the animal fats separated from them have a strong, rancid odour. It is noteworthy that when cocoa-nut oil alone is treated with carbon bisulphide and sulphur chloride, it behaves like butter; but when mixed with most fats or oils it is not so easily acted on by sulphur chloride, unless in large excess; by applying the author's method (*loc. cit.*) to an experimental mixture, containing 1 part of cocoa-nut oil to 3 parts of cotton-seed oil, the former oil was recovered perfectly white and solid. An example is given of the working of the method, applied to the analysis of an oleomargarine containing cotton-seed oil; and in two test experiments with the cotton-seed oil (as used in the analysis) alone, solid residues were obtained differing from one another by 5 per cent.; in the author's opinion, however, the difference need not be so great after a little practice. D. A. L.

Action of Sulphur Chloride on Oils. By T. T. P. B. WARREN (*Chem. News*, **57**, 26—27, 43).—The result produced by this reagent with linseed oil depends on the quality and quantity of the chloride, on the temperature at which the mixing is made, and on the quality and quantity of the solvent. If the solvent is volatile, inactive, and in excess, the reaction only starts when the sulphur chloride solution becomes sufficiently concentrated by the evaporation of the solvent. If the solvent is not volatile, the sulphur chloride reaction seems to be arrested or modified. Small quantities of sulphur chloride will merely thicken linseed oil owing to the altered oil dissolving in the unattacked oil, although oil once perfectly acted on will not dissolve in fresh oil. When analysing a mixture of drying with non-drying oils by means of sulphur chloride, it is well to add enough of a known oil to make the combined quantity of known and drying oil relatively large as compared with the non-drying oil. Under exactly similar conditions of experiment, a drying oil will yield constant quantities of a solid product insoluble in carbon disulphide; in the same way turpentine, resin oils, and mixtures of these yield products soluble in carbon bisulphide or heavy petroleum, therefore these latter oils can be readily separated from drying oils by sulphur chloride. As excess of sulphur chloride produces a less solid product than when such excess is avoided, this must be taken into consideration when treating unknown oils. In dealing with mixtures of oils in which each individual oil gives a solid product, the results obtained are only approximate, and must be verified by treatment of a known mixture of the oils. The author then indicates the very extensive amount of adulteration and substitution of inferior for superior oils in commerce, which can be detected by means of sulphur chloride. D. A. L.

Estimation of Urea by Titration. By T. Pfeiffer (*Zeit. Biol.*, **24**, 336—350).—This paper is a lengthy reply to the criticisms recently passed by Pflüger (this vol., p. 201) on Pfeiffer's modification of Liebig's method of estimating urea. W. D. H.

Titration of Pyridine Bases. By K. E. Schulze (*Ber.*, **20**, 3391).—5 c.c. of pure pyridine (sp. gr. 0·98) was dissolved in 100 c.c. of water; 25 c.c. of the solution was treated with 1 c.c. of 5 per cent. aqueous ferric chloride solution; normal sulphuric acid solution was then carefully added until the precipitated ferric hydroxide redissolved. The amounts actually used were 15·5, 15·4, and 15·5 c.c.; 15·5 c.c. being the amount required by theory. γ-Picoline was titrated in a similar manner. N. H. M.

Volatile Alkaloïds. By O. de Coninck (*Compt. rend*, **105**, 1258—1260).—A description of colour and other reactions of the pyridic alkaloïds.

Improved Method of Estimating Caffeïne in Coffee. By E. D. Smith (*Chem. Centr.*, 1887, 1270—1271; from *Zeit. öster. Apoth. Ver.*, **41**, 359).—To determine caffeïne, 0·65 gram of coarsely powdered coffee is mixed with 0·13 gram of magnesia, boiled with 150 c.c. of water for five minutes, filtered, and the filtrate made up to 200 c.c. by percolation; the residue is again boiled for five minutes with 100 c.c. water, filtered, and this filtrate made up to 300 c.c. by percolation. The combined filtrates are evaporated to 20 c.c., the residue treated with 120 c.c. of strong alcohol, the precipitate filtered and washed with alcohol, the alcohol driven off, and the residue dissolved by the gradual addition of small quantities of water. This solution is extracted three times with 25 c.c. of chloroform. On evaporating the chloroform, crystalline caffeïne is obtained. J. P. L.

Estimation of Theïne in Tea. By B. H. Paul and A. J. Cownley (*Pharm. J. Trans.* [3], **18**, 417—419).—The authors recommended the following method of estimating theïne (caffeïne) in tea:—5 grams of the powdered tea is moistened with hot water, mixed with 1 gram of calcium hydroxide, and dried on the water-bath. The residue is then extracted with strong alcohol in a small percolator. The alcohol is removed from the filtrate by evaporation, and the residual aqueous solution mixed with a few drops of sulphuric acid, filtered, and the filtrate shaken in a separator with about 200 c.c. of chloroform, which is used in six successive portions, the last being tested to ascertain that all the theïne has been taken up. The whole of the chloroform solution is then shaken in a separator with a very dilute solution of aqueous soda, by which it is completely decolorised; the chloroform extract is evaporated in a tared flask, and the residue weighed.

The authors have found in Indian and Ceylon teas a higher percentage of theïne than has usually been supposed to exist, varying from 3·22 to 4·66 per cent. on the air-dried substance. The amount of theïne had no relation to the commercial value of the 28 samples examined, the prices of which ranged from 7*d.* to 7*s.* per lb. The numerical results are given in a table. The method used by dealers in testing tea (tasting) is described. The value is not indicated by the amount of extract obtained by boiling water.

R. R.

Estimation of the Alkaloïds of Conium. By R. A. Cripps (*Pharm. J. Trans.* [3], **18[illegible]**, 511—512).—In place of the troublesome and inaccurate distillation methods, a process is described based on the extraction of the finely powdered fruits with a mixture of alcohol, chloroform, and a chloroform solution of hydrogen chloride, and the conversion of the bases in the extract into the hydrochlorides, in which form they are weighed.

A. J. G.

Determination of Tannin. By F. Gantter (*Zeit. anal. Chem.*, **26**, 680—682).—The author has made comparative determinations of tannin in a variety of tanning materials by the method of the German Tanners' Association (known as the 1 c.c. method), using on the one hand hide powder, and on the other the N/10 solution of ferric acetate recommended by E. B. (Abstr., 1887, 311). In almost every case, the latter gave the lower result, and from the fact of the quantity of substance taken being varied according to its richness, the differences are inversely proportional to the weights employed. In a nearly pure tannin, the difference amounted to 10 per cent. Unless, therefore, it can be shown that the precipitation by hide powder gives incorrect results, that by ferric acetate cannot be substituted for it.

M. J. S.

Hoppe-Seyler's Soda-test for Carbonic-Oxide-Hæmoglobin. By E. Salkowski (*Zeit. physiol. Chem.*, **12**, 227—228).—The following method of performing the test is suggested:—The blood in question is diluted 20 times, and to some of this in a test-tube an equal volume of aqueous soda of sp. gr. 1·34 is added. In a few seconds, carbonic oxide blood becomes whitish, then red; on standing, red flocculi separate, and finally rise to the surface of a faintly rose-coloured liquid. In normal blood, all that is produced by the addition of the alkali, is a dirty-brown coloration. After standing 20 hours, the precipitate in both cases is redissolved, and the clear red liquid shows almost the same absorption-bands as those of oxyhæmoglobin.

W. D. H.

General and Physical Chemistry.

Refraction of Liquids between wide Limits of Temperature. By E. KETTELER (*Ann. Phys. Chem.* [2], 33, 353—381 and 506—534).—As none of the expressions hitherto proposed for the refraction of liquids at different temperatures are found satisfactory, the author has from theoretical considerations deduced a relation between refraction and temperature, and tested the same experimentally. The first part of the paper is devoted to a description of the apparatus used and the method of working, in the second are the results of the experiments and a discussion of the same. The liquids examined were water and alcohol. The refraction in every case was measured for the sodium, lithium, and thallium lines.

The refraction of water between 0° and 20° having already been measured by Rühlmann, the present experiments were conducted for the interval 20° to 95°, a large number of observations at intermediate temperatures being made. The formula proposed by Rühlmann for the refractive index, $v = v_0 - at^2 + bt^4$, is found to be in fair agreement with the observed values up to 85°. A much better agreement is, however, obtained by the use of the author's proposed formula

$$(n^2 - 1)(v - \beta) = C(1 + \alpha e^{-kt}) = M,$$

where $C = (n^2 - 1)v = 0{\cdot}62035$, is taken from Lorenz's measurements for water-vapour and the sodium line. Also, since it is now proved that the dispersion for liquids follows the same law as that for gases, $\dfrac{n^2_\alpha - 1}{n^2_\beta - 1} = \text{const.}$, where for the same density α and β represent two different coloured rays; the constant C will alone alter with the nature of the light of which the other constants will be independent. For the lithium and thallium lines, C has the values 0·61574 and 0·62428. The equation is also satisfied by two series of values for the other constants, β, α, and k.

$$\begin{array}{llll} & (1)\ \beta = 0{\cdot}20271 & \alpha = 0{\cdot}00246 & k = 0{\cdot}02290 \\ \text{or} & (2)\ \beta = 0{\cdot}15999 & \alpha = 0{\cdot}05617 & k = 0{\cdot}000937 \end{array}$$

Both these series give values agreeing very well with the experiments, and the two agree well together up to 100°. For the latter series, k is so small that its higher powers may be neglected, and we get $M = C\ \{1 + \alpha(1 - kt)\}$, or the law of refraction takes a linear form with regard to t : $(n^2 - 1)(v - \beta) = c - \gamma t$.

For alcohol, the experiments extend from $-7{\cdot}85°$ to $+76{\cdot}34°$. A law similar to that in the case of water holds good. It is, however, not continuous, and two portions of the series have to be distinguished. Between $t = 33{\cdot}69°$ and $t = \infty$ we get $M = C\ (1 + \alpha e^{-k(t - t_0)})$, where the value of C for the lithium, sodium, and thallium lines is 0·84198, 0·84750, 0·85249; $t_0 = 33{\cdot}69°$, $\beta = 0{\cdot}200$, $\alpha = 0{\cdot}07748$, and

$k = 0{\cdot}002215$. From $t = -10°$ to $t = 33{\cdot}69°$, we get the simpler law $M = C(1 + \alpha)$, the value of which is 0·91317 for the sodium line.

In each case, the experiments prove that the dispersive power for the liquid and gaseous states is the same. H. C.

A New Method for Determining the Rotatory Dispersion of an Active Substance and a Case of Anomalous Dispersion. By G. H. v. Wyss (*Ann. Phys. Chem.* [2], **33**, 554—569).—The spectrum from ordinary white light is directed into a polarising apparatus by means of a collimator, the slit of which is adjusted to allow successively the passage of rays from each portion of the spectrum. The wave-lengths of the rays are calculated by means of Cauchy's formula. In this way, the rotation for different portions of the spectrum and for known wave-lengths is obtained.

A sample of turpentine thus examined was found to be feebly lævorotatory. It gave for $\lambda = 661$ a rotation of 3·0815°. As the wave-lengths decreased, the rotation increased and reached a maximum of 3·3688° for $\lambda = 565$. The rotation now, however, began to decrease on approaching the blue end of the spectrum, and for $\lambda = 494$ was only 2·9976°.

This behaviour is contrary to Biot's law that the rotation of a ray is inversely proportional to the square of the wave-length, an exception to which, however, had already been observed by Biot and Arndtsen in the case of tartaric acid, the latter concluding that the sample examined was probably a mixture of lævo- and dextro-rotatory acid. As it was quite possible that the present anomaly might arise from a similar cause, mixtures of dextro- and lævo-turpentines in different proportions were examined, and it was indeed found that a mixture containing about 68 per cent. of dextro-turpentine behaved in a manner exactly similar to the above. H. C.

Comparing Spectra. By E. F. J. Love (*Phil. Mag.* [5], **25**, 1—6).—In order to discriminate coincidences between lines of different spectra, a method based on the law of error is made use of, in which the differences between the wave-lengths of the compared lines are divided into groups according to the magnitude of the difference. A curve is then plotted having the number of observations in a group for an ordinate, and the average error of the group for an abscissa. The curve is compared with that given by the equation $y = a\epsilon^{-c^2x^2}$, and any large discrepancies noted. The above law supposes the errors to be of every magnitude and infinite number, hence the observed curve will be steeper than the theoretical one. Comparisons by this method of spectra of the same element obtained by different observers give curves which agree closely with the curve of error, whilst that obtained by a comparison of iron with nickel and titanium is widely divergent. A comparison between the arc-spectrum of cerium and the widened lines of a sun-spot spectrum gave a curve closely resembling the above test curves. Grünwald's comparison (Abstr., 1887, 1070) between the wave-lengths of the water-spectrum as deduced by him from those of hydrogen and their values as obtained by observation, is examined. The curve obtained agrees almost exactly with the theoretical curve except at four points. Finally, a comparison between the spectrum of Grünwald's constituent "*b*" of hydrogen and the nearest solar lines gives a curve which agrees with theory except at two points. The discrepancies in the two last comparisons seem to point to a small systematic difference, probably between the scale of measurement of the hydrogen spectrum and Ångström's scale.

H. K. T.

Modifications in the Absorption-spectrum of a Substance. By F. STENGER (*Ann. Phys. Chem.* [2], **33**, 577—586).—The absorption of light by any substance of definite chemical composition is assumed to depend on the size of the physical molecules of that substance in the condition in which it is examined. Hence as long as the molecular aggregation remains the same, whatever condition the substance be in, the absorption-spectrum will be the same, but an alteration in the molecular aggregation will bring about an alteration in the absorption-spectrum.

Iodine dissolves in carbon bisulphide to a violet, in alcohol to a brown solution. As the colour of the carbon bisulphide solution approaches more nearly to that of iodine vapour than that of the alcoholic, it may be assumed that in the first the molecules are in a simpler state of aggregation, and this view is supported by Wiedemann's observation that when the carbon bisulphide solution is cooled by means of ether and solid carbon dioxide, the colour changes to brown.

Magdala-red has a very different absorption-spectrum in alcohol, in which it is very soluble, to that which it shows in water, benzene, toluene, xylene, turpentine, or carbon bisulphide, in which it is only sparingly soluble. By mixing any of the latter solvents, however, with alcohol in different proportions, the absorption-spectrum of the one may gradually be converted into that of the other. The molecular aggregation in the first case where the substance is readily soluble is probably simpler than in those in which it is sparingly soluble.

Vogel (*Berl. Monatsber.*, 1878, 409) has shown that when a solution of a coloured substance or salt is evaporated on a glass plate, the absorption-spectrum of the solid obtained is very different from that of the solution. This alone greatly supports the view as to the influence of molecular aggregation. The author shows that if the solution be mixed with collodion, gelatin, or starch-paste and then evaporated, the character of the absorption-spectrum does not alter with the change from the liquid to the solid state. The above substances would appear to keep the molecules apart when drying, and prevent further aggregation taking place.

The above also holds good of those substances which show fluorescence in the liquid but not in the solid state. If solutions of such substances in gelatin be evaporated, the film fluoresces strongly even after it has been kept for some time. As fluorescence probably depends on the smallness of the physical molecules of the fluorescent substance, this further supports the author's views. H. C.

Fluorescent Mixtures. By L. DE BOISBAUDRAN (*Compt. rend.*, 452—455).—The author withdraws the statements made in *Compt. rend.*, **105**, p. 1231, lines 19—33, and p. 1232, lines 1—4. The quantities of chromium oxide given on p. 1229 are four times as great as they should be.

Purified calcium oxide shows distinct although not very strong greenish or bluish-white fluorescences, which are usually of short duration, and show no spectral bands. These fluorescences are much feebler after the calcium oxide has been strongly heated in hydrogen. Some specimens show a rose fluorescence which is not affected by heating in hydrogen.

Comparatively pure calcium carbonate was dissolved in hydrochloric acid, and fractionally reprecipitated. The first fraction showed a rose fluorescence, becoming blue-violet when heated, the manganese band being readily recognisable; the second fraction gave a blue-violet fluorescence, whilst in succeeding fractions the fluorescence became weaker and weaker. It would seem from these results that the fluorescence of calcium oxide is due to the presence of minute quantities of impurities. C. H. B.

Galvanic Polarisation. By F. STREINTZ (*Ann. Phys. Chem.* [2], **33**, 465—474).—In continuation of his experiments on the above (this vol., p. 99), the author has examined the polarisation of mercury, gold, palladium, and platinum electrodes. With mercury, the polarisation of the hydrogen plate is at a maximum when the E.M.F. of the cell used is that of two Daniells, and for further increase remains constant. This maximum is higher than that observed for any other metal. The polarisation of the oxygen plate varies with the time of immersion, and continually increases with the E.M.F. of the cell used. With the three other metals, the results agree generally with those of Fromme (Abstr., 1887, 541). When the intensity of the current used is greater than that required to produce maximum polarisation, in each case a decrease in that of the oxygen plate sets in, that of the hydrogen plate remains constant in the case of platinum, but shows a variation with the time of immersion for gold and palladium.

H. C.

Conductivity of Illumined Air. By S. ARRHENIUS (*Ann. Phys. Chem.* [2], **33**, 638—644).—It is shown that air under a pressure of 1 to 20 mm., when illumined by the sparks of an electrical machine, acts as a conductor, the maximum conductivity being for a pressure of 4 to 5 mm. This conductivity is shown to be electrolytic, as a current may be obtained flowing from a zinc to a platinum plate in illumined air, just as it would were these plates immersed in water. No manifestation of the above could be obtained for pressures other than those stated, although the author considers that it is not confined within those limits. In support of this he quotes the experiments of Hertz (*Ann. Phys. Chem.* [2], **31**, 983), in which it was shown that sparks are more easily formed in air at the ordinary pressure when the path is illumined than when it is kept in the dark.

H. C.

Molecular Conductivity of Fuming Nitric Acid. By E. Bouty (*Compt. rend.*, **106**, 595—597).—Fuming nitric acid, which always contains a slight excess of water, dissolves large quantities of potassium nitrate, forming compounds which can be crystallised, and the solutions behave with respect to conductivity like aqueous solutions of very soluble salts. The conductivity of the acid at first increases more rapidly than the proportion of dissolved salt, attains a maximum, and then decreases as the solution becomes more viscous. With small quantities of salt, the increase in conductivity is proportional to the weight of salt dissolved.

Sodium nitrate is only slightly soluble in nitric acid, and does not form crystallisable compounds. The nitric acid solution, like the aqueous solution, behaves abnormally, and has a higher resistance than similar solutions of other nitrates.

The unit of conductivity in these experiments was the resistance of normal nitric acid. The nitric acid used was of sp. gr. 1·552. A molecular resistance of 15·72 ohms is the limit of conductivity of the solutions of potassium and ammonium nitrates in nitric acid. This value approximates very closely to the molecular resistance of potassium chloride in aqueous solution. The resistance of solutions of nitrates in nitric acid increases rapidly on addition of water.

C. H. B.

Electrical Resistance of Bismuth and its Alloys. By E. v. Aubel (*Phil. Mag.* [5], **25**, 191—201).—The electrical resistance of bismuth and its alloys in a powerful magnetic field is determined. The bismuth was prepared in three forms—(1) melted and cooled slowly; (2) melted and cooled quickly; (3) compressed. The first was obtained by melting the metal in capillary tubes immersed in sand; for the second the metal was melted and poured into a V-shaped iron mould; the third was prepared by Spring's method. The alloys were prepared by mixing weighed quantities of the metals. The resistances were measured by Thomson's method, and the results show that in some samples of bismuth the resistance rises, in others falls, with rise of temperature. The experiments with alloys show that this is not due to the presence of tin or arsenic as an impurity, nor was there any relation shown with their fusing points or specific gravities. Magnetism produces an increase in resistance, but the effect is feeble. Compressed bismuth shows hardly any alteration in resistance with change of temperature, but if it is fused and cooled slowly the usual effect is observed. In the compressed bismuth which had been drawn through a draw-plate, the particles form parallel fibres.

H. K. T.

Electrolysis of Copper. By T. Gray (*Phil. Mag.* [5], **25**, 179—184; compare Abstr., 1887, 315).—The electrochemical equivalent of copper is determined for varying current-densities. The copper sulphate solutions had a density of 1·15 to 1·18, and were always acid. The plates were cleaned with glass-paper, and after deposition were washed with acidified water and dried before a fire. At temperatures of 10—15°, the results are constant, but the loss in weight of the plate increases rapidly as the temperature rises to 35°. The error can be ascertained within 0·1 per cent. by keeping a similar plate in a cell with no current passing through it. At 2°, there is no change in the amount of metal deposited until the area of the plate exceeds 200 sq. cm. per ampère. A table of apparent electrochemical equivalents of copper for different current-densities and temperatures is given. H. K. T.

Thermal and Electrical Behaviour of some Bismuth-tin Alloys in the Magnetic Field. By A. v. ETTINGSHAUSEN and W. NERNST (*Ann. Phys. Chem.* [2], **33**, 474—492).—The authors were led by former experiments to suspect some connection between the thermoelectrical properties of metals, and the "rotatory power" in a magnetic field observed by Hall (*Phil. Mag.*, 1885, **19**, 419). Since the thermoelectrical properties of bismuth are greatly modified by alloying with tin, the present investigations were undertaken with the object of ascertaining whether this modification would be attended with similar change in the rotatory power. A series of four alloys containing varying amounts of tin were examined, but although the rotatory power was very largely influenced by the presence of the tin no definite connection with the thermoelectrical properties could be traced. H. C.

The Recalescence of Iron. By H. TOMLINSON (*Phil. Mag.* [5], **25**, 103—116).—The internal friction of iron at different temperatures is determined by suspending a wire vertically and noting its period of horizontal vibration, the wire being heated by an electric current. A table of results is given. At 550° the internal friction rises rapidly, and still more rapidly at 1000°, so that at this temperature the wire comes to rest after two or three vibrations. From 1100° to 1200° it seems to decrease. At 550° the magnetic and thermoelectric properties also change. At 1000° heat also becomes latent, as shown by alterations at this temperature due to stress and strain. The author considers that recalescence is similar to regelation, being a sudden evolution of heat at temperatures somewhat below these points. When iron has been strained either by bending or hammering, the strained portion as the iron cools appears clouded, owing to the more rapid cooling of the strained portion, its specific heat being less than that of the unstrained parts, probably because the consumption of heat in separating the particles is prevented by the strain. Shortly before recalescence, the cloud disappears. Recalescence does not seem to be prevented by shaking or hammering. With well annealed iron, recalescence cannot be detected. The author considers that it does take place, but at a point near the critical temperature (1000°), and hence is not visible. H. K. T.

Evaporation of Liquids. By W. HEMPEL (*Ber.*, **21**, 900—902).—Liquids can be evaporated about six times more rapidly (with, however, the combustion of about three times the amount of gas per hour) than on a steam-bath by employing a Siemens' inverted regenerative burner placed just above the surface. The liquids do not enter into ebullition, so all spirting is avoided. Experiments show that no appreciable amount of sulphuric acid is absorbed by the liquids during evaporation, and that whilst hot the iron parts of the burner are not attacked by acid vapours. W. P. W.

Bumping during Distillation. By A. Reissmann (*Arch. Pharm.* [3], **25**, 970; from *Pharm. Centralb.*, **28**, 501).—A closely wound platinum spiral is charged with several longish bits of pumice, and its ends are then closed. One or more of these spirals placed in a liquid undergoing distillation effectually prevents bumping, and the operation goes on with perfect regularity. The platinum must be heavy enough to sink the pumice. J. T.

Relation of Gases to Mariotte's Law at High Temperatures. By C. Puschl (*Monatsh.*, **9**, 93—98).—If at ordinary temperatures the volume of a liquid be v and the pressure p, pv increases with the pressure, so that $d(pv)/dp = h$ is positive. If t be the temperature, and α the coefficient of expansion of the liquid, then $dh/dt = d(\alpha pv)/dp$, so that by following the change in h with temperature, the change in pv or in Mariotte's law may be ascertained.

At pressures above the critical, heating the liquid gradually to above the critical temperature, the quantity h will be found to pass through two maxima with one minimum in between, and the latter if the pressure be continually increased at high temperatures will change from negative to positive values, and may in the end be brought into coincidence with the higher maximum, which at the same time falls to lower temperatures. If the pressure then were high enough, h would, from the lower maximum, continually decrease with rise of temperature.

For pressures below the critical, h is negative and increases with the temperature. This is the case with all gases and vapours, with the exception of hydrogen. If heated, then, a point $h = 0$ will be reached at which the gas will obey Mariotte's law. Above this point, h takes a positive value, reaches a maximum, and then falls again, it crosses the zero-line a second time, and becomes permanently negative.

There is also for every gas an interval of temperature for which h is positive at every pressure, and pv has neither maximum nor minimum. On each side of this interval, there are two pressures for every temperature at which $h = 0$, for the smaller of which pv is a maximum and for the greater a minimum. At the higher and lower limiting values for these temperatures the two pressures will coincide. H. C.

Easy Method of Finding the Specific Gravity of Liquids. By A. B. Taylor (*Chem. News*, **51**, 138—139).—For the sake of simplicity, the author suggests that the weight of a convenient solid should be so adjusted that, expressed in grains, it corresponds with its sp. gr., then, on weighing it in the liquid to be tested, the loss of weight in grains will give the sp. gr. of that liquid without calculation. D. A. L.

Compressibility of Water. By W. C. RÖNTGEN and J. SCHNEIDER (*Ann. Phys. Chem.* [2], **33**, 644—660).—The authors repeat their experiments on the above (*Ann. Phys. Chem.* [2], **29**, 197), using greater pressures, and thus obtaining a greater contraction. The apparatus, with the exception of a new manometer, is that previously used. Experiments were conducted at the temperatures 0°, 9°, and 17·95°, and gave as the apparent compressibility per atmosphere at these temperatures 0·00004910, 0·00004602, and 0·00004413. The experiments being made with great care, and account taken of all known sources of error, the last figure only in the above is looked on as doubtful. The constant of deformation of the piezometer was determined by comparing the observed apparent compressibility of rock salt with the true compressibility obtained by Voigt (*Ber.*, 1884, 990); by introducing this correction, the true compressibility of water at the above temperature is obtained. This is 0·0000462 at 17·95°, a value which exactly agrees with that obtained by Grassi, 0·0000481 at 9°, and 0·0000512 at 0°. H. C.

Decrease in the Solubility of Sulphates. By A. ETARD (*Compt. rend.*, **106**, 206—208).—At temperatures below 100°, the solubility of cupric sulphate increases with the temperature, but between 103° and 190° the solubility diminishes as the temperature rises. This deflection in the curve of solubility is observed with almost all sulphates. With cadmium, zinc, manganese, and iron sulphates, the point of deflection is below 100°. A similar decrease in solubility is observed in the case of salts of carbonic, sulphurous, and succinic acids, but not with salts of monobasic acids, except those of feeble organic acids.

In the case of zinc sulphate, $y = 27·6 + 0·2604t$ between $-5°$ and 81°, and $y = 50·0 - 0·2244t$ between 81° and 175°. At 180°, the solubility is the same as at $-5°$. As the temperature of a saturated solution rises, the hydrate $ZnSO_4 + 2H_2O$ is deposited on the sides of the vessel in hard, insoluble, porcelain-like concretionary masses. At all temperatures there is, in all probability, a condition of equilibrium between this and the other hydrates existing in the solution.

In the case of manganese sulphate, $y = 30·0 + 0·2828t$ between $-8°$ and 57°, and $y = 48·0 - 0·4585t$ between 57° and 150°. The solution deposits anhydrous manganese sulphate as a hard, rose-coloured, porcelain-like mass, almost insoluble in water. The equation indicates that the solubility vanishes at 161°, and experiment shows that at 180° the liquid retains mere traces of the salt.

For potassium sulphate, $y = 7·5 + 0·1070t$ between 0° and 163°, and between 163° and 220° the solubility remains constant.

C. H. B.

Laws of Chemical Equilibrium. By H. LE CHATELIER (*Compt. rend.*, **106**, 355—357).—A mathematical paper, not admitting of useful abstraction.

Chemical Equilibrium. By P. DUHEM (*Compt. rend.*, **106**, 485—487).—The results obtained by Le Chatelier are identical with those obtained by the author (*Compt. rend.*, **99**, 1113).

Laws of Chemical Equilibrium. By H. LE CHATELIER (*Compt. rend.*, **106**, 598—601).—The author points out that there is an essential difference between his views and those of Duhem.

C. H. B.

Explosion of Water Gas. By A. v. OETTINGEN and A. v. GERNET (*Ann. Phys. Chem.* [2], **33**, 586—609).—The gas generated electrolytically was passed without previous drying into the eudiometer, and by means of a rotating mirror photographs of the course of the explosion were taken, small quantities of metallic salts being used to colour the flame. The results show that in accordance with Bunsen's view, the total combustion takes place in successive partial explosions. Each explosion causes a wave which travels along the tube, and the meeting of two such waves gives rise to secondary waves, as appears from the photographs. The rate of explosion measured was 2800 metres per second, which agrees approximately with the value obtained by Berthelot.

H. C.

The Carbon-atom and Valency. By V. MEYER and E. RIECKE (*Ber.*, **21**, 946—956).—The theoretical conclusions of van't Hoff and Wislicenus have not only been supported but also extended by the experiments of Meyer and others on the isomeric benzildioximes; the result of which is, that to the hitherto generally accepted properties of the carbon-atom, the following two must be added :—(1) The four valencies of the carbon-atom can be diverted from the regular tetrahedric direction in which they are supposed to exist in marsh-gas, and compounds of the constitution Ca_4; (2) There are two ways in which two singly-bound carbon-atoms can be united, one which allows free rotation in various directions, one which does not.

On various chemical and physical grounds, the authors put forth the following hypothesis on the constitution of the carbon-atom :—The carbon-atom is surrounded by an ethereal shell which, in the case of an isolated atom, has a spherical form; the atom itself is the carrier of the specific affinities, the surface of the shell is the seat of the valencies; each affinity is determined by the existence of two opposite electrical poles, which are situated at the end-points of a straight line small in comparison with the diameter of the ethereal shell. Such a system of two electric poles is called a double- or dipole. The four valencies of a carbon-atom would be represented by four such di-poles, the middle points of which are situated on the surface of the ethereal shell, but freely movable within it. The dipoles themselves can rotate freely round their middle point. The carbon-atom has a greater attraction for positive than for negative electricity, and the positive pole of a valency is slightly stronger than the negative pole.

This hypothesis would explain—Why the four valencies take up the position of a regular tetrahedron; why they can be diverted from this position; why the valencies of one and the same carbon-atom cannot combine together, whilst the valencies of different carbon-atoms can do so; why there are two kinds of single-binding, (1) one stable, (2) and the other allowing free rotation; and lastly, why free rotation ceases in cases of double- or treble-binding.

F. S. K.

On Valency. By H. E. ARMSTRONG (*Phil. Mag.* [5], **25**, 21—30). The author extends Helmholtz's theory that the valency of an atom corresponds with the number of charges of electricity with which it is associated (Trans., 1881, 277) by supposing that "molecular" combinations are due to the same cause. As instances of substances which may be looked on as molecular compounds, the author quotes the tetralkyl-compounds of ammonium. The stability of the iodides of these bases in the presence of potassium hydroxide is such as is shown by no other iodide except those of carbon; they fully resemble in this respect methyl iodide and iodobenzene. Moreover, although the heat of neutralisation of tetramethylammonium hydroxide is equal to that of potash whilst that of methyl alcohol is small, in the latter case the combination is incomplete and in many cases the salt produced is insoluble and does not interact with water. In aniline, the basic properties, so far from being entirely dependent on the nitrogen-atom, are lessened and ultimately almost annulled by the introduction of halogens into the phenyl radicle. Some hydrazines are monobasic, others bibasic, although they all contain two (triad) nitrogen-atoms: hence, the pentad nature of the nitrogen in the salts of these substances is doubtful, and they are better considered as so-called molecular compounds. To explain these molecular combinations, the charge of electricity is supposed to penetrate the atom and to have varying degrees of freedom of motion. In some combinations, such as H_2, the opposite charges approach one another, and there is no residual affinity; whilst in others, such as HCl, the charges of some of the atoms do not move towards those of their neighbours, their influence is not entirely neutralised and a residual affinity obtains. In tetramethylammonium iodide, the nitrogen of the molecule NMe_3 has such a residual affinity which is neutralised by a similar residual affinity in the iodine of the methyl iodide. Ammonium haloïd compounds, in that they can further combine with halogens, show residual affinity, but it is not probable that the halogen of the ammonium salt serves as the bond of union. On the other hand, in the double metallic salts the halogen does play this part, and from their analogy to ammonium haloïd compounds the halogen in the latter should serve as the bond of union. In view of this conflict of evidence, the theory of the ammonium radicle is questioned, and the perhalogen-compounds are regarded as formed by the union of the halogen with the nitrogen-atom —a view supported by the fact that ammonium sulphate combines with halogens. That the same result is obtained in whatever order the radicles are inserted in a tetralkylammonium-compound may be due to isomeric change at the moment of formation, and does not necessarily prove the atomic constitution of these compounds. In the case of phosphorus, the existence of the compound PF_5 does not prove its quinquavalence in face of the compounds H_2F_2 and HFFR, which prove that fluorine can combine with itself. Instead of the constitution $Cl_2P{\cdot}OCl$ for phosphorus oxychloride, the oxygen may be considered to be united to the phosphorus-atom in PCl_3 by residual affinity. For bismuth, the compound $BiPh_3Br_2$ only proves that it belongs to the nitrogen-phosphorus-group so long as its constitution is unknown. In the compounds $PbEt_4$ and $TeCl_4$ the lead and tellurium atoms may be considered to have charges showing little mobility, hence each charge binds two monad atoms. The elements of the carbon-silicon-group are probably tetrads, whilst iron in the ferric compounds is a triad. Chlorides in which the chlorine-atoms form a closed chain are also conceivable. From the above it follows that, except in the paraffins, benzenes, and their haloïd and alcoholic derivatives, the constitution of compounds is by no means settled, and that a more liberal interpretation of facts than heretofore must be made. H. K. T.

Tetravalency of Oxygen. By J. F. Heyes (*Phil. Mag.* [5], **25**, p. 221—237).—The author considers that molecular compounds of haloïd salts can be better explained by supposing the haloïds to be trivalent than by grouping the atoms round a central atom, which must, therefore, have a very high valency. This, with the occasional tetravalency of oxygen, gives formulæ for the oxychlorine acids more in accord with their properties than those in use. Thus potassic hypochlorite becomes $K—Cl\equiv O\equiv O\equiv Cl—K$, whilst the substances $KClO_3$, $KClO_4$ may be looked upon as $K—Cl\equiv$ united to groups of oxygen-atoms $(O_3)''$ or $(O_4)''$, forming perhaps a closed chain.

The tetravalence of oxygen is supported by the peroxides, BaO_2,MnO_2, whose properties, distinct from those of SnO_2,SiO_2, point to a composition $X''\equiv O\equiv O$, and by the oxides of silver, mercury, and copper. Sodium dioxide, since it is not decomposed by heat, is considered to have the structure $Na—O—O—Na$, whilst in K_2O_4 there is an (O_4) nucleus related probably to that in $KClO_4$ and Cl_2O_4. The interaction of water with organic substances such as aldehyde, acetal and acetic acid, favours the view of the occasional tetravalency of oxygen, as do also the gaseous acetic acid molecule $(C_4H_8O_4)$ of Ramsay and Young, and Friedel's substance, $(CH_3)_2O,HCl$. The double metallic oxides, basic salts, and water of crystallisation $(—OH_2{\cdot}OH_2{\cdot}OH_2—$, &c.) also favour this view. In substances where there are two valencies the author proposes the term validity to indicate the less powerful affinity: thus chlorine is monovalent and trivalid; carbon is tetravalent, except in CO and CNO, where it is bivalid. J. J. Thomson has pointed out that according to the vortex theory a dyad might unite not only with two atoms but also with four atoms of a monad, so that water consists of three primaries $H_2—O—O$. The author's formula, $H_2\equiv O\equiv O$, agrees with this theory and also with Brodie's $H_2\overset{+}{O}\overset{-}{O}$. As an instance of a radicle at once mono- or tri-valent, the author quotes $(C_3H_5)'''$, which if regarded as an atom is analogous to gold or thallium. H. K. T.

Investigation of the Second van't Hoff Hypothesis. By K. Auwers and V. Meyer (*Ber.*, **21**, 784—817).—This vol., p. 597.

Simple Procedure for the Determination of Molecular Weights by Raoult's Method. By A. F. HOLLEMANN (*Ber.*, **21**, 860—862).—The simplifications introduced proceed on the same lines as those already described by V. Meyer and by K. Auwers (this vol., pp. 407—409).

Ancient Process for making Gems and Glasses Phosphorescent. By BERTHELOT (*Compt. rend.*, **106**, 443—446).—An extract from ancient Greek MSS. containing recipes for making gems, glasses, &c., phosphorescent, or imparting to them more brilliant colours, by coating them with thin layers of various-coloured or phosphorescent substances, the latter being usually of the nature of readily oxidisable organic compounds. C. H. B.

Inorganic Chemistry.

Rate at which Bleaching Powder loses its available Chlorine when kept at Different Temperatures. By J. PATTINSON (*J. Soc. Chem. Ind.*, **7**, 188—191).—It is shown that although the available chlorine of bleaching powder disappears in proportion to the length of time it is kept and to the temperature to which it is subjected, yet, within a comparatively small amount, the whole of the chlorine it originally contained is still retained in some form or other in combination with the calcium of the compound. This, at any rate, is true of bleaching powder when kept in casks or bottles for about 12 months at temperatures varying from 15·5° to 26·5°. D. B.

Preparation of Tetrathionates from "Wackenroder's" Solution. By T. CURTIUS and F. HENKEL (*J. pr. Chem.* [2], **37**, 137—149; compare Debus, Trans., 1888, 278).—When "Wackenroder's" solution is shaken for a considerable time with excess of barium carbonate and then filtered, the solution is quite clear, neutral to litmus, and contains sulphur and barium present in the ratio of four atoms of the former to one of the latter, thus corresponding with barium tetrathionate. If, however, the solution is imperfectly neutralised it will contain acid tetrathionates, and consequently sulphur will be present in a quantity larger than that represented by the ratio S_4:Ba. The existence of these acid tetrathionates, unknown until now, has led many investigators to wrongly assert that polythionic acids, containing more sulphur than tetrathionic acid, are present in Wackenroder's solution. Pure barium tetrathionate may be obtained from Wackenroder's solution, which has been completely neutralised by barium carbonate, by precipitating with alcohol and then alternately dissolving in water and precipitating with absolute alcohol. As thus prepared, the salt is identical with that formed by the action of iodine on the thiosulphate, and has the formula $BaS_4O_6 + 2H_2O$.

If Wackenroder's solution is neutralised by means of the carbonates of zinc and manganese, and then an equal volume of the solution added, acid salts of these metals are obtained. These acid salts are much more stable than the normal ones, and dissolve readily in cold absolute alcohol, from which they can be recrystallised over sulphuric acid in a vacuum. The zinc salt, $(S_4O_6H)_2Zn$, crystallises from alcohol in groups of small needles, is somewhat hygroscopic, and is exceedingly soluble in cold water and in cold alcohol. It decomposes at a little above 100°, and addition of potash to the aqueous solution causes an immediate separation of sulphur. The manganese salt, $(S_4O_6H)_2Mn$, crystallises in rose-coloured plates, and in all its other properties much resembles the zinc salt. The authors have observed the peculiar appearance and properties of the sulphur present in Wackenroder's solution (Debus, *loc. cit.*). G. T. M.

Hydrofluorides of Potassium Fluoride. By H. MOISSAN (*Compt. rend.*, **106**, 547—549).—When dry, powdered potassium fluoride is gradually added to liquid anhydrous hydrofluoric acid it dissolves rapidly with development of heat, and if the solution is cooled to −23° it yields highly hygroscopic crystals of the hydrofluoride of potassium fluoride, KF,3HF. This compound gives off hydrogen fluoride in moist air, and dissolves rapidly in water with liberation of acid and great reduction of temperature. When heated, it loses hydrogen fluoride and yields a residue of potassium fluoride. At 100°, the fused salt has no action on crystallised silicon, but if rapidly heated to a higher temperature the mixture becomes incandescent with violent evolution of silicon fluoride. The fused salt acts energetically on silica and decomposes carbonates. It is decomposed by sulphuric acid in the cold with very rapid evolution of hydrogen fluoride, and acts energetically on potash and ammonia.

If the potassium fluoride and hydrogen fluoride are mixed in suitable proportions, the compound KF,2HF is obtained; this is liquid at 105°, and on cooling forms crystals similar to those of the preceding compound. It may be kept liquid between 65° and 105°, and under these conditions acts readily on many minerals and organic substances.

These compounds are analogous to Berthelot's hydrochlorides of chorides and Troost's compounds of ammonia with ammonium salts. The trihydrofluoride is, however, somewhat stable, and decomposes very slowly in dry air or even in a vacuum. C. H. B.

Preparation of Cakes of Ammonium Chloride and Ammonium Carbonate. By W. HEMPEL (*Ber.*, **21**, 897).—When heated at 50—100° and subjected to hydraulic pressure, powdered ammonium chloride and ammonium carbonate are respectively converted into hard cakes. W. P. W.

Soluble Phosphates in Superphosphates. By H. OTTO (*Chem. Centr.*, 1887, 1563—1564; from *Zeit. Chem. Ind.*, **2**, 207—210).—The solubility of the pure calcium salt, $CaH_4(PO_4)_2$, in water at 15° is about 1 in 25. Solutions of the phosphate do not undergo decomposition at the ordinary temperature; at 50°, slight decomposition begins, and at 90° $CaHPO_4$ is precipitated, free phosphoric acid going into solution.

Acid phosphate of iron, $FeH_6(PO_4)_3$, is decomposed by water at the ordinary temperature into $FePO_4$ and free phosphoric acid; the greater the volume of water, the more complete the decomposition. Acid phosphate of aluminium on the other hand does not decompose, but dries to a white, colourless mass, again soluble in water. It decomposes on heating. Acid phosphate of manganese, which occurs in some superphosphates, forms a bright rose-coloured, crystalline product, which is easily soluble in water, and is not decomposed even by large quantities of water.

The whole of the soluble phosphates of aluminium and manganese existing in superphosphate are dissolved in estimating the soluble phosphates.

In consequence of the decomposition which acid phosphate of iron undergoes, and the partial decomposition between the iron and monocalcic phosphates, the soluble phosphate obtained by the process recommended by the Magdeburg Conference (namely, extraction with a large volume of water at once, 1,000 c.c. to 20 grams superphosphate) is considerably less than that obtained by the usual process of extracting with successive small quantities.

A comparison of the two methods with a superphosphate containing 49·9 per cent. P_2O_5 gave the following result: Magdeburg method, 45·8 per cent. P_2O_5; usual method, 47·2 per cent. P_2O_5.

J. P. L.

Anhydrous Magnesium Chloride. By W. Hempel (*Ber.*, **21**, 897).—Crystallised magnesium chloride can be rendered anhydrous and the formation of basic salt prevented by heating it in a current of hydrogen chloride.

W. P. W.

Instability of the Double Sulphates, $M''SO_4$, $R'_2SO_4 + 6H_2O$, of the Magnesium Series. By W. Dittmar (*Proc. Roy. Soc. Edin.*, **124**, 219—220).—When to a solution of a known weight of potassium sulphate, dissolved in a quantity of hot water less than sufficient to hold the intended double salt in solution, a known weight of the bivalent sulphate amounting to exactly 1 or 1·1, 1·2—1·5MgO, or FeO per $1K_2O$, is added, the resulting crystals are found to be coated with potassium sulphate; with 1·2 or 1·3MgO per $1K_2O$, the crystals become more and more pure. The results with ferrous sulphate are similar.

E. W. P.

Action of Potable Water on Lead Pipes. By E. Reichardt (*Arch. Pharm.* [3], **25**, 1049—1052; compare this vol., p. 344).—Present experience shows that waters which act on lead pipes, generally, if not exclusively, contain free carbonic anhydride. The view that lead pipes gradually become coated internally so as to resist this action is still wanting proof. It has been ascertained that the addition of finely-powdered calcium carbonate suffices perfectly to prevent the action; the free carbonic anhydride quickly attacks the carbonate, leaving any excess undissolved.

J. T.

Corrosion of Leaden Water Pipes. By T. CARNELLEY and W. FREW (*J. Soc. Chem. Ind.*, **7**, 15—20, and 78).—The results show that the corrosion is much greater with free exposure to the air than by exclusion of the latter; the action of water being diminished to about one-fourth, and that of calcium hydroxide to about one-fifth, when air is excluded. This confirms the observations of previous investigators. The most important result, however, is the great protective action exerted by sand, calcium carbonate, old mortar, calcium silicate, and a mixture of sand and calcium carbonate. The circumstance that the presence of sand has a most important effect in protecting lead from corrosion has already been shown by Crookes, Odling, and Tidy, in a report on the action of water on lead made to the Water Committee of the Corporation of Huddersfield in 1886. In this report, it is shown that the action of soft water on lead is regulated by the amount of silica contained in the water, and also that the most effectual way to silicate a water is to pass it over a mixture of flints and limestone. They do not, however, give any reason or experiment to show why a mixture of these two should be more effectual than either alone. The authors are of opinion that the true explanation is to be found in the formation of calcium silicate, and as a proof assign the fact that calcium silicate itself, either as such or in the form of old mortar, is more effective than either calcium carbonate or silica separately (compare Müller, this vol., p. 225, Reichardt, p. 344, and preceding Abstract). D. B

Displacement of Copper by Zinc. By A. DESTREM (*Compt. rend.*, **106**, 489—492).—Pure zinc introduced into solutions of copper salts with strong acids produces a brown or blackish slightly adherent deposit of copper. In slightly alkaline solutions, the deposit is red and firmly adherent. In the case of copper salts of feeble acids the deposit has the colour of brass and is strongly adherent, especially if the solution is electrolysed for a short time with an anode of metallic copper.

Pure carefully cleaned zinc was immersed for brief equal intervals of time in solutions of cuprammonium sulphate, cupric acetate, cupric formate, and cupric picrate. At first the weight of the zinc increases, but afterwards it gradually diminishes with each successive immersion and tends to become constant. If there were simply an exchange of copper for zinc, the weight of the zinc should always decrease. The yellow colour of the deposit, its firm adherence to the zinc, and the increase in weight indicate that on the first immersion of the zinc into neutral or feebly alkaline solutions, alloys of zinc and copper resembling brass are formed. If the yellow deposit is touched with a rod moistened with hydrochloric acid, the red colour of copper appears, owing to the more rapid dissolution of the zinc. When the solution of the copper salt is acid, there is no increase in the weight of the zinc.

Similar phenomena are observed in the case of cadmium.

C. H. B.

Action of Sulphur Vapour on Copper. By H. N. WARREN (*Chem. News*, **57**, 95).—If sulphur is thrown on to molten copper and the mass allowed to cool when the reaction has ceased, a button is produced consisting of a core of pure copper enclosed in a uniform shell of copper sulphide; the thickness varying with the quantity of sulphur employed. In a similar manner, a rod of copper 1 inch in width was exposed at a dull red heat for half an hour to the action of sulphur vapour, in this case also, a layer of copper sulphide of uniform thickness was formed, leaving a core of pure copper. Good commercial copper must be used. D. A. L.

Absorption of Carbonic Oxide by Cuprous Chloride. By W. HEMPEL (*Ber.*, **21**, 898—900).—Cuprous chloride solution absorbs noteworthy quantities of all gases, and it is therefore necessary to saturate a fresh solution with those gases in a mixture with which it does not enter into combination, otherwise the diminution in volume is greater than that due to the absorption of carbonic oxide; the results of the first analysis in which this solution is employed should consequently be rejected. When once saturated, the cuprous chloride solution gives very concordant results with gaseous mixtures whose composition is tolerably constant as, for example, with coal-gas. If, however, a solution, which has been used with one kind of gas, is employed for the analysis of a mixture of different composition, errors come in owing to the evolution of a portion of those dissolved gases which are absent from or are present in smaller proportions in the new mixture, and to the absorption of others; it is on this account that Drehschmidt found that the volume of the hydrogen increased in his experiments (this vol., p. 88; *Ber.*, **20**, 2753). W. P. W.

Basic Aluminium Sulphate. By C. BÖTTINGER (*Annalen*, **244**, 224—227).—A basic aluminium sulphate of the composition $Al_2O_3,SO_3,6H_2O$, is deposited when a solution containing 5 grams of aluminium sulphate and 1½ grams of common salt is heated at 140° in sealed tubes. It is insoluble in water, and loses 2 mols. H_2O at a dull red heat. W. C. W.

Preparation of Potassium Manganate. By A. JOLLER (*Arch. Pharm.* [3], **25**, 970; from *Rep. anal. Chem.*, 1887, No. 33).—Potassium hydroxide (2 mols.) is placed in a crucible, some water is added, and finely divided potassium permanganate (2 mols.) is gradually added with constant stirring and heating. After two hours at a faint red heat, the crucible is cooled, and the manganate placed in a well-stoppered flask to prevent access of air and contact with organic matter.

The value of manganate as a reagent depends on its solubility in alkalis without change. The alkaline solution has the greatest tendency to produce with certain oxides precipitates which settle rapidly, and are constant in composition. Again, the solution is so powerful an oxidising agent that certain compounds are readily and perfectly oxidised at ordinary temperatures, whilst permanganate frequently requires heat and a large excess of reagent. Lastly, the end of the reaction is sharply defined, the green colour disappears, and the solution becomes colourless. J. T.

Combination of Carbon with Iron under Pressure. By W. HEMPEL (*Ber.*, **21**, 903).—When tested for its tensile strength, steel is found to give a fracture which is grey in the centre and brighter in colour towards the edge, whilst a fracture of the same specimen obtained in the ordinary way without extension has a uniform appearance. Inasmuch as contraction occurs in the former case previous to fracture, the author considers that owing to the resulting pressure a portion of the carbon present passes into the combined form (compare Spring and van't Hoff, this vol., p. 341), and ascribes the increase in the hardness of iron which occurs in wire-drawing or when it is hammered cold to a similar cause. W. P. W.

Cobaltic Alums. By H. MARSHALL (*Proc. Roy. Soc. Edin.*, **123**, 203—204).—When mixed solutions of cobalt sulphate and ammonium or potassium sulphate are electrolysed in a divided cell so arranged that the two electrodes are practically in separate vessels, the solution changes to greenish-blue, due to the oxidation of the cobaltous to a cobaltic compound. After crystallisation, a blue ammonium alum is obtained, which when dry is stable, but in solution rapidly becomes reduced, the oxygen which is liberated being in part ozone. A potassium alum was obtained but with less ease, but the salt was always mixed with potassium sulphate from which it could not be freed. Nickel salts of a corresponding composition have not hitherto been obtained. E. W. P.

New Hydrate of Molybdic Acid. By A. VIVIER (*Compt. rend.*, **106**, 601—602).—White crystals of the composition H_2MoO_4, separated from a solution of ammonium molybdate in nitric acid They may also be obtained by heating the ordinary molybdate solution at 50—60° with its own volume of water for several days.

C. H. B.

Titanium Chloride and Titanic Acid. By R. WAGNER (*Ber.*, **21**, 960—962).—Commercial titanium chloride has always a yellowish or greenish colour; the former is usually due to ferric chloride, the latter to chlorine and sometimes to certain decomposition products of titanium chloride. A little stannic chloride was found in one sample, but with this exception, no foreign element other than iron could be detected. Chlorine, hydrochloric acid, and ferric chloride can be removed by slow distillation over sodium, other impurities are eliminated by fractional distillation.

A clear solution of orthotitanic acid can be obtained by adding water, in small quantities at a time, to titanium chloride, the mixture being well shaken during the process.

The hydrate of orthotitanic acid, precipitated in the cold from a clear solution in hydrochloric or sulphuric acid, yields, when dried in the air or at a moderate temperature, not only a white but also a green, brown, or black hydrate according to the treatment adopted; the latter is the final product of the orthohydrate.

When moist orthotitanic acid is heated, a remarkable play of colours is observed, and the oxide on further careful heating becomes almost white, but appears citron-yellow while hot; by continued heating, the colour becomes more and more brownish. Metatitanic acid becomes brownish-coloured when ignited for a quarter of an hour.

If orthotitanic acid is allowed to remain under water for a long time it is partially converted into metatitanic hydrate.

The colour of titanium dioxide depends on the treatment to which it has been subjected. F. S. K.

Action of Vanadic Anhydride on Alkaline Fluorides. By A. DITTE (*Compt. rend.*, **106**, 270—272).—Sodium fluoride when heated in a closed crucible with an excess of vanadic anhydride yields a crystalline, red mass, and when this is treated with tepid water, it yields an orange solution, which deposits orange-red crystals of the composition $3V_2O_5,4NaF + 18H_2O$. The mother-liquor when concentrated yields lemon-yellow crystals of the compound $V_2O_5,4NaF$. With an excess of the alkaline fluoride, the product is pale-yellow, and is only slowly attacked by water. If extracted with warm water and the solution evaporated in a vacuum, the compound $3V_2O_5,4NaF + 18H_2O$ is obtained in transparent, orange-red crystals, and the mother-liquor yields small, yellowish-white crystals of the compound $V_2O_5,8NaF + 3H_2O$.

If a boiling saturated solution of sodium fluoride is mixed with excess of soluble vanadic anhydride and filtered, the filtrate deposits brilliant red crystals of the compound $V_2O_5,NaF + 5H_2O$, and the mother-liquor yields brilliant, lemon-yellow crystals of the compound $V_2O_5,6NaF + 5H_2O$. All these sodium compounds are analogous to those previously obtained with potassium fluoride.

A warm concentrated solution of ammonium fluoride dissolves a large quantity of soluble vanadic anhydride, and the warm liquid deposits the compound $V_2O_5,4NH_4F + 4H_2O$ in pale-yellow crystals, very soluble in water. When heated, they lose water and hydrogen fluoride, and yield the compound $V_2O_5,2NH_4F$. If the mother-liquor from the first crystals is mixed with excess of vanadic anhydride, filtered and cooled, it deposits the compound $V_2O_5,4NH_4F + 4H_2O$ in almost white, brilliant, nacreous needles, readily soluble in cold water. With a cold solution of ammonium fluoride and excess of vanadic anhydride, the first product consists of indistinct yellow crystals of the composition $V_2O_5,8NH_4F + 4H_2O$, followed by crystals of the compound $V_2O_5,4NH_4F + 4H_2O$.

Vanadic anhydride reacts with many other metallic fluorides, and the products are under investigation. C. H. B.

Action of Hydrogen Chloride on Cupric Chloride. By ENGEL (*Compt. rend.*, **106**, 273—275).—Hydrochloric acid precipitates cupric chloride from its solution in accordance with the author's law—that is to say, the sum of the equivalents of acid and salt in solution remains practically constant. At first the sum of the equivalents slightly diminishes, but when 10 c.c. of the solution contains 70 equivalents of hydrogen chloride the law is exactly obeyed. Beyond this point, the sum of the equivalents increases slowly as the proportion of free acid increases.

If a solution of cupric chloride is saturated with hydrogen chloride at 20—25° and then cooled to 0°, it deposits a hydrochloride of cupric chloride, $CuCl_2,HCl + 3H_2O$, in deep, garnet-red needles which lose hydrogen chloride and become green when exposed to air. Decomposition soon ceases in a closed vessel, and the crystals remain unaltered in an atmosphere of hydrogen chloride.

Dihydrated cupric chloride, $CuCl_2 + 2H_2O$, absorbs hydrogen chloride and becomes garnet-red, water being liberated. This fact, together with the colour of the hydrochloride, seems to indicate that the water is combined with the hydrogen chloride, and the cupric chloride is present in the anhydrous condition. The brown colour of a solution of cupric chloride containing much free hydrochloric acid is probably due to the presence of the hydrochloride.

It is noteworthy that all hydrochlorides of chlorides hitherto described contain water of crystallisation. C. H. B.

Preparation of Auroso-auric Chloride. By J. THOMSEN (*J. pr. Chem.* [2], **37**, 105—108).—Krüss and Schmidt have recently (this vol., p. 28) denied the existence of auroso-auric chloride, Au_2Cl_4. The failure of their attempts to obtain it is considered to be due to the necessary temperature not having been maintained. Definite directions are now given for its successful preparation. By leading a stream of dry chlorine for 30 minutes over gold, precipitated from a solution of gold chloride by sulphurous acid, 50 to 70 grams of gold may be converted into a homogeneous mass corresponding with the formula Au_2Cl_4. The reaction is started by gentle heating, but the necessary temperature is then maintained by the heat evolved in the reaction, provided that cooling is prevented by surrounding the tube with cotton or glass-wool. G. T. M.

Ruthenium Peroxide. By H. DEBRAY and A. JOLY (*Compt. rend.*, **106**, 328—333).—The instability of ruthenium peroxide prepared by the ordinary method is due to the presence of a small quantity of water. In order to obtain the oxide in a perfectly anhydrous condition it is enclosed in a tube which is contracted at the middle, one-half being filled with fused calcium chloride. When the tube is made vacuous, the ruthenium peroxide gradually sublimes, and that part of the tube which contains it is separated from the remainder by fusion and the oxide redistilled in a vacuum. The tubes in which it is preserved should be carefully cleansed from organic matter, and then dried by heating to redness whilst a current of hydrogen is passed through them.

Ruthenium peroxide melts at 25·5°, forming a deep orange-red liquid which solidifies slowly even in presence of crystals of the substance. The fused oxide remains vitreous for a long time, and can only be obtained in distinct crystals by sublimation, which takes place readily with very slight change of temperature under a pressure of 3 to 4 mm. It does not boil below 106°, and at 106—107° it decomposes. No ebullition was observed under any conditions. The vapour-tension is 183 mm. at 100·8°; 20 mm. at 42°, and practically *nil* at 0°. It may be distilled in water vapour if the latter contains chlorine or hypochlorous acid; vapour-density by Dumas' method at 100° under a pressure of 106 mm. = 5·77; calculated for Ru = 104, 5·81. The peroxide attacks mercury, and acts slightly on glass in diffused light.

Ruthenium peroxide dissolves in water, forming a golden-yellow solution which contains no definite hydrates. The pure solution may be kept for some time, even in diffused light, but gradually decomposes with evolution of oxygen and deposition of a black layer of the oxide, Ru_2O_3, which when dried above 100° contains 2 mols. H_2O. The exact amount of water, however, depends on the conditions of drying. The decomposition by water is more rapid the higher the temperature, and at 100° it rapidly becomes complete—brilliant black scales of the lower oxide, $Ru_4O_9,2H_2O$, being obtained. This oxide becomes anhydrous at 360° without loss of oxygen, but at 440° it is converted into the dioxide. The oxide, Ru_4O_9, is also obtained by heating the oxide, $Ru_2O_5,2H_2O$, in a dry vacuum at a temperature not exceeding 360°.

The peroxide is stable below 106°, but at 107° sudden decomposition takes place with production of a smoky flame, the liquid portion being converted into the crystallised dioxide, whilst a pulverulent form of the same oxide is deposited on the sides of the tube. Decomposition is complete, but there is no actual explosion.

It has previously been shown (this vol., p. 426) that the peroxide is formed by the oxidation of the dioxide at 1000°, and it is evident that the relation between the dioxide and peroxide is similar to that existing between water and hydrogen peroxide. C. H. B.

Mineralogical Chemistry.

Gold, Alunite, and Sulphur from New South Wales, and Native Antimony from Queensland. By R. W. E. MACIVOR (*Chem. News*, **57**, 64).—Gold occurs at Gumdagai, in New South Wales, in fine flakes irregularly distributed through a matrix of serpentine, and varying in quantity from a few pennyweights to several ounces per ton. The serpentine is associated with an abundance of asbestos, and appreciable quantities of gold have also been found in some specimens of the latter mineral. Sulphur and alunite, yielding its own weight of alum perfectly free from iron, have been found in considerable quantities in Gloucester Co., N.S.W. The alunite is generally quite white, but sometimes has a very slight pinkish hue, probably due to a trace of manganese.

The author has examined some very pure specimens of antimony from Northern Queensland; all seemed to be water-worn, and some consisted of the metal only, others of the metal associated either with calcium carbonate or quartz. D. A. L.

Stromeyerite from Zacatecas in Mexico. By G. A. KÖNIG (*Jahrb. f. Min.*, 1888, i, Ref., 190, from *Proc. Acad. Nat. Sci. Phila-*

delphia, 1886, 281).—The specimen analysed consisted of long, prismatic crystals, with broken ends, planted on quartz. The mineral has no cleavage; its colour is iron-grey, its hardness 3·5, and its sp. gr. 6·23. Analysis gave the following results:—

S.	Cu.	Ag.	Insoluble.	Total.
15·81	33·69	50·18	0·26	99·94

which corresponded with the formula CuAgS. B. H. B.

New Mineral in the St. Bernard Lode at Hausach. By F. V. Sandberger (*Chem. Centr.*, 1887, 1568—1569, from *Öst. Zeit.*, 35, 528—533).—The new mineral, which the author names *Metalonchidite*, consists of rhombic crystals like radiating pyrites, but distorted in the macrodiagonal axis, with irregular fracture, and hardness = 7; sp. gr. = 5·08. They are of zinc-white colour, and metallic lustre, and give on analysis—

S.	As.	Fe.	Ni.	Cu.	Pb.	Ag.	Total.
49·56	2·73	45·12	1·29	0·72	1·12	0·11	100·551

If the mineral is regarded as an isomorphous mixture of FeS_2 with $FeAs_2$, the following formula, $25FeS_2 + 1Fe(Ni,Cu,Pb,Ag)As_2$, which nearly approaches the formula of the lonchidite,

$$(22FeS_2 + 1Fe(Co,Cu,Pb),$$

is obtained. The occurrence of silver and traces of gold and platinum in metalonchidite is worthy of notice. J. P. L.

Association of Fluorspar with Babel Quartz at Ville-Vieille, near Pont Gibaud. By F. Gonnard (*Compt. rend.*, **106**, 558—560).—The lead mines at Ville-Vieille yield crystals of fluorspar with crystals of quartz embedded in their surfaces. These quartz crystals are arranged more or less regularly *en échelon*, just as in many English specimens. The author considers that the mode of occurrence indicates that the crystallisation of the quartz was simultaneous with that of the fluorspar, and not subsequent to it. Similar relations were observed to exist between crystals of quartz and crystals of chalcopyrites from Weardale. C. H. B.

Caracolite and Percylite. By M. Websky (*Jahrb. f. Min.*, 1888, i, Ref., 202—203, from *Akad. Wiss. Berlin*, 1886).—At Carocoles, in Chili, the rare mineral, percylite, occurs in small, azure-blue cubes in association with colourless crystals of caracolite. The composition of percylite is expressed by the formula $Pb_2OCl + Cu_2OCl + xH_2O$, that of caracolite by the formula $HPbOCl + Na_2SO_4$. The sp. gr. of caracolite is approximately 5·1. The crystals, which appear as though hexagonal, belong really to the rhombic system. The axial ratio is 0·5843 : 1 : 0·4213. (Compare Sandberger, Abstr., 1887, 902.)

B. H. B.

Artificial Rubies. By E. Fremy and A. Verneuil (*Compt. rend.*, **106**, 565—567).—The rubies were obtained in the usual way by the action of barium fluoride on alumina mixed with traces of potassium dichromate. The regularity of crystallisation depends on the proper regulation of the temperature. The product is a porous, friable mass, filled with geodes containing the rubies, which are separated by levigation. The rubies form transparent, regular, rhombohedral crystals of a red colour, which become dark on heating, but lighter again on cooling, like the natural gem. They are as hard as natural rubies, and scratch topaz. C. H. B.

Mineralising Action of Alkaline Sulphides: Formation of Cymophane. By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, **106**, 487—489).—Alkaline sulphides fused in a carbon crucible dissolve alumina at a dull red heat, and at higher temperatures crystals of corundum are obtained. The presence of an alkaline carbonate retards the mineralising action, and a greater proportion of the alumina forms soluble compounds.

Beryllia likewise dissolves in fused alkaline sulphides, and is converted into crystals, the proportion converted into soluble compounds being less than in the case of alumina, and independent of the presence or absence of alkaline carbonates. The crystals of beryllia thus obtained are colourless, transparent, and uniaxial, with positive compensation. The common form is a hexagonal pyramid, modified by faces on the edges of one of the bases, but the exact form depends on the temperature, and also on the presence or absence of alkaline carbonates.

A mixture of alumina and beryllia when dissolved in fused alkaline sulphides yields crystals with all the physical and chemical characteristics of cymophane. They are colourless and slightly opalescent, rhombic plates with a brilliant, adamantine lustre. Good results are obtained with a mixture of 100 parts of alumina, 40 parts of beryllia, 650 parts of potassium sulphate, and 150 of carbon. The product is treated with acidified water, and the uncombined beryllia is removed by treatment with warm, dilute, sulphuric acid and the carbon by calcination. Cymophane is always obtained, even in presence of a large excess of alumina and a very small quantity of beryllia. If an excess of beryllia is present, it becomes crystalline. Alkaline carbonates reduce the yield of cymophane and increase the proportion of crystallised beryllia. C. H. B.

Jacobsite from the Sjö Mine. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1888, i, Ref., 184, from *Bull. soc. franç. min.*, **10**, 170—174).—In the Sjö mine, Örebro, Sweden, microscopic crystals of jacobsite are found in calcite in the veins of hausmannite, associated with scheelite, polyarsenite, pyrrhoarsenite, tephrite, and iron glance. This jacobsite contains more manganous oxide than the jacobsites of Langban and Jacobsberg. The best analyses gave the following results:—

	Mn_2O_3.	Fe_2O_3.	MnO.	Total.
I.	18·42	51·54	30·04	100·00
II.	12·84	56·25	30·91	100·00

I after deducting 0·9 per cent. of tephrite; II after deducting 2·5 per cent. of tephrite and 4·9 per cent. of calcite. B. H. B.

Jacobsite from Nordmarken. By L. J. Igelström (*Jahrb. f. Min.*, 1888, i, Ref., 184, from *Bull. soc. franç. min.*, **10**, 184—186).—Compact masses of jacobsite from Nordmarken in Sweden have the composition expressed by the formula $Mn_3O_4 + 2Fe_3O_4 + 6MnO,Fe_2O_3$, which is somewhat analogous to that of the franklinite of New Jersey. The percentages found by the author on analysis were—

Fe_2O_3.	Mn_2O_3.	MnO.
68·86	8·00	23·14

The percentage of ferrous oxide found is not stated.

B. H. B.

Two Varieties of Goethite from Saône et Loire. By A. Lacroix (*Jahrb. f. Min.*, 1888, i, Ref., 182—183, from *Bull. soc. franç. min.*, **8**, 41).—At Chizeuil the author has found chocolate-brown to yellow, fibrous goethite having the following composition:—

Fe_2O_3.	H_2O.	Total.	Sp. gr.
87·0	13·0	100·0	4·32

This mineral the author classes as lepidocrocite. At Romanèche, small geodes of hæmatite are covered with a velvety, chestnut-brown layer resembling the goethite of Przibram. B. H. B.

Pseudomorphs after Marcasite. By E. Cohen (*Jahrb. f. Min.*, 1888, i, Ref., 174—175, from *Situngsber. nat. Vereins Neu-Vorpommern u. Rügen*).—The concretions of marcasite, usually unaltered, in the chalk of Rügen are at Arkona altered, and form a brownish-yellow substance resembling yellow ochre. Usually all the marcasite has disappeared, and the concretion forms a pseudomorph, in the interior of which the radial structure of the marcasite may be detected. Analysis gave the following results:—

SiO_2.	SO_3.	Fe_2O_3.	H_2O.	Loss on ignition.	Total.
9·30	4·30	66·80	6·70	13·72	100·82

The substance thus appears to be a mixture of 9·88 silica, 11·93 copiapite, and 78·19 limonite. B. H. B.

Occurrence of Epsomite on White Island, New Zealand. By R. W. E. Macivor (*Chem. News*, **57**, 114; compare this vol., p. 427).—Epsomite, $MgSO_4,7H_2O$, is met with in many places as an efflorescence on the gypsum-covered floor of the crater. It contains a distinct trace of ferrous sulphate. D. A. L.

Mineralogical Notes. By F. A. Genth (*Jahrb. f. Min.*, 1888, i, Ref., 187—188, from *Proc. Amer. Phil. Soc.*, **24**, 23).—1. *Mimetesite pseudomorphous after Anglesite.*—These crystals occur with the reniform tinstone of Durango, Mexico, and exhibit the combination $\breve{P}\infty$, $\frac{1}{2}\bar{P}\infty$. Analysis gave the following results:—

As_2O_5.	P_2O_5.	PbO.	CaO.	Cl.	Ignition.
24·97	0·05	71·40	0·57	7·47	0·37

Together with 0·65 per cent. of clay and tin oxide.

2. *Vanadinite.*—Analyses are given of vanadinite from, I, Pinal Co., Arizona (brown); II, Pinal Co. (orange); III, Yavapai Co., Arizona (olive-green).

	V_2O_5.	As_2O_5.	P_2O_5.	PbO.	CuO.	Cl.	Fe_2O_3.	Less O.	Total.
I.	16·98	3·06	0·29	77·49	—	2·41	0·48	0·55	100·16
II.	17·16	4·30	trace	77·47	—	2·46	—	0·56	100·83
III.	18·64	trace	0·72	77·96	0·18	2·69	0·04	0·61	99·62

3. *Cuprodescloizite*, from San Luis Potosi, Mexico, occurs as a radiated incrustation 1 to 10 mm. thick, of a yellowish-brown colour and resinous lustre. Sp. gr. 6·203. Analysis gave—

V_2O_5.	As_2O_5.	P_2O_5.	PbO.	CuO.	ZnO.	H_2O.	Total.
19·99	3·63	0·13	54·52	6·58	12·70	2·62	100·17

These numbers are in accord with the formula of descloizite, $(PbCuZn)_2OH(VAsP)O_4$, and confirm the accuracy of the former analyses of this mineral by Rammelsberg and Penfield.

4. *Pseudomorphs of iron pyrites after magnetic pyrites*, from Sulphur Creek, Colusa Co., California. The occurrence of iron pyrites in small, hexagonal tablets, 1 mm. in diameter, with rough basal planes and smooth prism planes, is regarded as a pseudomorph after magnetic pyrites.

5. *Hessite* from the West Side Mine, Tombstone, Arizona, occurs in quartz with cerargyrite and grains of gold. Sp. gr. 8·359. Analysis gave—

Ag.	Pb.	Te.	Total.
62·87	0·28	37·34	100·49

6. *Tapalpite* from the Sierra de Tapalpa, Mexico. This rare mineral occurs with iron pyrites, galena, quartz, and silicates. From analyses of impure material, the formula $Ag_3Bi(TeS)_3$ is deduced. The sp. gr. of the pure mineral is 7·75.

7. *Allanite* from Statesville, North Carolina, occurs with zircon crystals. It is brown-black in colour, has a sp. gr. of 3·63, and gave on analysis the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	$Ce_2O_3 + Di_2O_3 + La_2O_3$.	$Y_2O_3 + Er_2O_3$.	FeO.	MnO.
31·68	17·33	7·05	18·99	1·12	10·11	1·03

CaO.	MgO.	Na_2O.	H_2O.	Total.
10·78	0·54	0·21	1·46	100·30

B. H. B.

Pyrrhoarsenite, a New Mineral from the Sjö Mine. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1888, i, Ref., 184—185, from *Bull. soc. franç. min.*, 9, 218—220).—This mineral occurs with barytes, tephroite, calcite, and hausmannite in narrow veins in the Sjö Mine. Optically it resembles the berzeliite of Langban. Its hardness is 4. Analysis gave the following results:—

$As_2O_5 + Sb_2O_5$.	MnO.	CaO.	MgO.	SiO_2.	H_2O.	Total.
58·06	17·96	18·68	3·58	1·02	0·85	100·15

The mineral is thus an antimony-bearing berzeliite rich in manganese, and having the formula $(CaMnMg)_3(AsSb)_2O_8$ (compare Abstr., 1887, 902). B. H. B.

Pleochroism of Biotite. By E. COHEN (*Jahrb. f. Min.*, 1888, i, Mem., 165—169).—In cordierite and in muscovite, it is easy to prove by heating that the pleochroic borders first described by Rosenbusch are due to organic matter. In biotite, however, this phenomenon can only be explained with difficulty, heating with a Bunsen burner giving a negative result. This fact has induced Michel-Lévy and others to conclude that the pleochroic portions of biotite are due, not to organic matter, but to a concentration of ferriferous mica molecules. In biotite of the granite-porphyries and gneisses of Urbies in Lower Alsace, such pleochroic borders are extremely abundant, and a number of sections have been examined by the author. When a thin section that has been carefully cleaned with ether is treated with dilute hydrochloric acid at a gentle heat, a period will be reached in which the biotite becomes considerably lighter in colour, although the pleochroic border presents no change. Even when the biotite is completely bleached, as long as the structure and double refraction remain, the pleochroic border will be unchanged. The latter disappears only when the section is strongly heated and then treated with dilute hydrochloric acid until the transparency is recovered. These experiments show that the pleochroic borders in biotite are due to organic matter whose decomposition requires a higher temperature than that of muscovite or of cordierite. B. H. B.

Manganese-zinc-serpentine from Franklin, New Jersey. By G. A. KÖNIG (*Jahrb. f. Min.*, 1888, Ref. 189, from *Proc. Acad. Nat. Sci. Philadelphia*, 1886, 355).—The material analysed was a compact, dark-brown serpentine, which in thin section exhibited a few grains of franklinite and of garnet. The analytical results were as follows:—

SiO_2.	MgO.	MnO.	ZnO.	H_2O.	Franklinite.	Pyroxene.	Total.
41·70	29·24	6·91	3·10	14·04	4·15	1·05	100·16

B. H. B.

Chrysocolla from California. By E. JANNETAZ (*Jahrb. f. Min*, 1888, i, Ref., 183—184, from *Bull. soc. franç. min.*, 9, 211—213).—A specimen of opal mixed with the hydrated copper silicate contained

13 per cent. of water. The mixture had the following percentage composition:—

SiO_2.	CuO.	H_2O.	Fe_2O_3.	CuCl.	$CaCO_3$.	Total.
49·1	30·4	18·0	1·2	0·9	0·5	100·1

In thin sections, the copper silicate appears in radiated fibres having the same optical character (negative) as a dioptase cut perpendicular to its axis. Chrysocolla from Chili and from Siberia exhibit similar optical characters. B. H. B.

Analysis of Chiastolite. By W. Müller (*Jahrb. f. Min.*, 1888, i, Ref., 175—176).—The author gives the following analysis of 0·1447 gram of chiastolite from the Alexandovski mine at Nertschinsk:—

SiO_2.	Al_2O_3.	Fe_2O_3.	Loss on ignition.	Total.
34·85	62·28	0·85	0·89	98·87

Very similar results are obtained on analysing the andalusite of Brazil. B. H. B.

Sanidinites from São Miguel. By A. Osann (*Jahrb. f. Min.*, 1888, i, Mem., 117—130).—The sanidinites examined form part of the series collected in the Azores by Reiss and Hartung. Their structure is holocrystalline-granular. There is no amorphous cementing material, and no trace of porphyritic structure. Among the constituents of the rock, sanidine predominates, then follows hornblende or sometimes augite. All the rest, including mica and quartz, are subordinate. The accessory minerals are sodalite, zircon, pyrrhite, lavenite, titaniferous iron ore, and apatite. The sanidine is colourless and glassy, and on analysis gave the following results:—

SiO_2.	$Al_2O_3 + Fe_2O_3$.	CaO.	Na_2O.	K_2O.	Total.	Sp. gr.
65·74	20·26	0·25	6·63	6·14	99·02	2·57

With regard to their geological occurrence and their mineralogical composition, the sanidinites form well-characterised rocks. At the Laacher See, in the Rhone, at Vesuvius, and at São Miguel, they always occur in the form of loose blocks, and have never been found in place. B. H. B.

Copper Ores containing Tourmaline from Tamaya in Chili; Geological Occurrence of Boron Minerals. By A. v. Groddeck (*Chem. Centr.*, 1887, 1518—1519, from *Zeit. Geol. Ges.*, **39**, 237—266).—The tourmalines are of microscopic size (0·1 to 0·5, in exceptional cases 2 mm. long, 0·05 to 0·1 mm. broad). They occur in (1) copper sulphides (copper pyrites, purple copper ore, and copper glance), (2) in the oxidised copper ores at the outcrop of the lode, (3) in the lode minerals (calcite and quartz), (4) in the matrix. An analysis gave—

SiO_2.	Al_2O_3.	B_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.
36·34	32·22	10·87	8·31	0·79	3·92	3·14	0·22	3·89

Total.	Sp. gr.	
99·70.	3·2.	Traces of fluorine.

A calcite from the Murciélagos mine of an anthraconite colour proved to be mixed with copper glance and tourmaline. In round numbers, 22 per cent. of copper glance, 36 per cent. tourmaline, and 42 per cent. calcite.

From the spathose, quartzose, micaceous, and chloritic matrix, and partition rocks of the lode, the following were submitted to analysis:—

I. A white, clear rock, consisting of 92 per cent. potash mica (sericite), 3 per cent. calcite, and 5 per cent. of silica (opal ?).

II. The pure mica of the foregoing rock, which, however, still contained some purple copper ore, chlorite, and opal (?)

III. A porphyritic rock, in the crystalline matrix of which quartz, orthoclase, plagioclase, and titanic iron were embedded.

IV. A rock similar in structure to No. III, the felspar and matrix of which are changed into a fine-grained aggregate of quartz, sericite, and carbonate.

V. A solid porphyritic rock, in the grey matrix of which plagioclase, magnetic iron ore, titanic iron, and hornblende are embedded.

VI. A decomposed porphyritic rock consisting essentially of quartz and mica minerals, but also containing some tourmaline.

	I.	II.	III.	IV.	V.	VI.
SiO_2...	43·88	42·61	75·93	63·85	59·54	66·44
Al_2O_3..	31·43	34·02	13·26	17·51	13·09	17·43
Fe_2O_3..	3·57	3·87	1·47	1·94	4·74	2·10
FeO ...	0·88	0·95	0·68	0·18	6·13	1·60
MnO ..	—	—	trace	trace	0·49	—
MgO ..	0·65	0·70	—	—	1·33	3·70
CaO ...	3·73	2·42	1·11	0·96	3·81	0·65
K_2O ...	10·35	11·20	3·19	4·77	3·86	4·76
Na_2O ..	2·01	2·18	3·13	0·25	5·88	0·99
H_2O...	1·89	2·05	0·44	1·02	0·68	2·13
CO_2 ...	1·17	—	0·51	8·41	0·18	0·10
Total ..	99·56	100·00	99·72	99·73	100·32	99·902

No. III contains traces of TiO_2; IV, 0·84 of copper pyrites; V, 0·59 P_2O_5; VI, traces of SnO_2 and P_2O_5.

Besides the rocks analysed, which may be perhaps regarded as dioritic porphyrites, gabbro was found under the Tamaya rocks, but pure diorite and syenite, which have been previously described, were absent. Tourmaline was absent from all the solid partition rocks, and they were free from boron. The mineral is limited to the lode, lode minerals, and matrix of the ore. The question of the formation of the lodes, whether by lateral secretion or by the rise of hot springs, the author leaves opens, but he considers the question of their formation from the activity of fumaroles to be excluded.

A geological grouping of boron minerals is also given.

J. P. L.

The Basalts of Alsace. By G. Linck (*Jahrb. f. Min.*, 1888, i, Ref., 235—236, from *Mitth. Commission geol. Landesunters. Elsass-*

Lothringen, 7, 49—68).—In Alsace, basalt occurs only in two places—at Reichshofen in Lower Alsace, and at Reichenweier in Upper Alsace. The basalt from the former locality is a felspar-basalt (Analysis I), whilst the basalt of Reichenweier is a limburgite (Analysis II), similar to that occurring at Forst in the Palatinate.

	SiO_2.	TiO_2.	Al_2O_3.	$FeO + Fe_2O_3$.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	52·60	0·57	14·17	11·38	9·17	6·37	1·06	2·90	2·08	100·30
II.	42·30	1·51	12·74	10·60	13·01	12·74	0·94	2·65	2·54	99·03

B. H. B.

Quartz Conglomerate from Witwatersrand, Transvaal. By P. HOLLAND (*Chem. News*, **57**, 76—77).—The Witwatersrand reefs consist mainly of loose quartz conglomerate varying in colour from light yellow to dark-reddish or purplish-brown. A specimen of the dark variety consisted of waterworn quartz pebbles and angular fragments of coarse-grained quartzose sandstone of various sizes, mixed with siliceous matrix material. Scales of mica were also detected, but there was no "visible gold." The sample as received contained slightly more than 15 dwts. of gold per ton; whilst those portions of the specimen passing through a ¼-inch mesh sieve (amounting to about half the original), contained about 1 oz. 3 dwts. of gold per ton, and had the following general composition:—

SiO_2.	Al_2O_3.	Fe_2O_3.	TiO_2.	MnO.	CaO.	MgO.	K_2O.	Na_2O.
85·72	4·27	6·18	0·12	0·03	0·01	trace	0·23	0·32

Organic matter.	Water.	Total.
0·29	2·56	99·73

The gold is found chiefly in the matrix material. D. A. L.

Chloritoïd-schist from Grossarl. By A. CATHREIN (*Jahrb. f. Min.*, 1888, i, Ref., 242, from *Tschermak's min. Mitth.*, **8**, 331—337).—In the Grossarl valley, Salzburg, a schist occurs containing numerous dark-green groups of chloritoïd crystals in a yellowish-white groundmass. The latter consists of quartz, rutile, titanite, iron pyrites, and titaniferous iron ore. The pulverised rock was boiled in dilute sulphuric acid, all the chloritoïd and ore together with some titanite and rutile passing into solution. The soluble part (I) and the insoluble (II) gave on analysis the following results:—

	SiO_2.	TiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
I.	25·50	1·88	38·69	27·19	0·40	0·08	6·67	100·41
II.	92·82	6·93	—	—	0·76	—	—	100·51

Calculated from I, the formula of the chloritoïd is approximately $H_2FeAl_2SiO_7$. The composition of the rock, calculated from I and II, is 63·98 per cent. of chloritoïd, 30·16 of quartz, 4·03 of rutile and ore, and 1·83 of titanite. Thus the proportion of chloritoïd is greater than in any chloritoïd schists known elsewhere. B. H. B.

Labrador-porphyries of the Vosges. By A. OSANN (*Jahrb. f. Min.*, 1888, i, Ref., 237—239; from *Abhdl. geol. Specialkarte Elsass-Lothringen*, **3**, pt. 2).—The so-called labrador-porphyries occur in the Southern Vosges, near the Sulzer Belchen, within a highly contorted series of culm rocks. The rocks examined by the author were found in the vicinity of Gebweiler, Masmünster, the Rossberg, Seewen, and St. Amarin. They have a brown, green, or grey colour, and consist principally of plagioclase and augite. The plagioclase appears to be labradorite, its extinction being 5° to 8° on 0P, and 19° to 24° on $\infty\breve{P}\infty$. The results of an analysis of unaltered plagioclase from the brown porphyry of the Rimbachthal were as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O_3.	K_2O.	Total.
54·09	28·98	0·94	9·13	5·19	1·19	99·52

From these results the author deduces the composition

$$2Or,14Ab,13An.$$

The augite in the rock is found by analysis to have an intermediate place between the diopside-like augites in granite and the augites in diabase. B. H. B.

Analysis of Shotley Bridge Spa Water. By H. PEILE (*J. Soc. Chem. Ind.*, **7**, 14).—The water when first collected is perfectly clear, but has a slightly brown tinge. It has a strong, ferruginous taste, which it loses on standing, when the taste of common salt may be readily detected. The sp. gr. at 15·5° is 1·00197, the temperature at the well 10°, the air at the time of observation being 14°. The water has for many years been used by persons suffering from rheumatism and skin diseases. The analysis of the water in grams per litre, and the percentage composition of the solid residue dried at 180° (2·484 grams per litre) gave—

	$BaCl_2$.	NH_4Cl.	$CaCl_2$.	LiCl.	$MgCl_2$.	KCl.
Water	0·0569	0·0042	0·2632	0·0065	0·0437	0·0513
Residue...	2·29	—	10·95	0·26	1·76	2·06

	NaCl.	$CaH_2(CO_3)_2$.	$CaCO_3$.	$MgH_2(CO_3)_2$.	$FeH_2(CO_3)_2$.
Water	1·7333	0·3964	—	traces	0·155
Residue...	69·77	—	11·08	—	—

	$MnH_2(CO_3)_2$.	Fe_2O_3.	$MgBr_2$.	MgI_2.	$MgCO_3$.	SiO_2.
Water	traces	—	0·0075	0·000056	—	traces
Residue...	—	0·62	0·30	0·002	traces	traces

	P_2O_5.	Mn.	Albuminoid NH_3.	Total CO_2.	Free CO_2.	Totals.
Water	traces	—	traces	0·3340	0·0833	—
Residue...	traces	traces	—	—	—	99·092

D. B.

Chemical Composition of the Water composing the Clyde Sea Area. By A. DICKIE (*Proc. Roy. Soc. Edin.*, **124**, 422—427).

Organic Chemistry.

Fire-damp. By B. FRANKE (*J. pr. Chem.* [2], **37**, 91--101, 113—136).—The author has made an elaborate series of experiments on the origin of fire-damp. Examination and analyses of many samples of gas taken from mines under different conditions show that they may be roughly classified, according to the nature of the gas contained in the coal, under the three following heads:—(1) Mines, the coal of which gives an incombustible gas consisting of much nitrogen and little methane. (2) Mines, the coal of which gives a combustible gas, not capable however of forming an explosive mixture with air. In such mines, the coal should be worked in ascending galleries and the efficiency of the ventilation occasionally checked by analysis of the air. (3) Mines, the coal of which gives gases rich in methane and forming explosive mixtures with air. In mines of this class, safety lamps must be used together with a perfect system of exhaust ventilation from every point at which coal is worked.

G. T. M.

Decomposition of Chloroform by Alcoholic Potash. By L. DE ST. MARTIN (*Compt. rend.*, **106**, 492—495).—A solution of potassium hydroxide in alcohol of 60° decomposes chloroform slowly but almost completely at the ordinary temperature, and decomposition is rapid at 100°. If the strength of the potash solution is known, the excess may be determined by titration, using phenolphthaleïn as indicator, and after the liquid has been carefully cooled the amount of the potassium chloride formed may be estimated by silver nitrate solution with potassium chromate as indicator. In the cold solution the alcohol and potassium formate have no effect on the titration. In order to employ this method for the estimation of chloroform, the latter is heated with the alcoholic potash in sealed tubes, and the excess of potash and amount of chloride formed are estimated.

In order to determine the quantity of chloroform vapour in air or other gases, a known volume of the gas is allowed to enter a vacuous globe into which a measured quantity of alcoholic potash is then introduced. After standing for eight or ten days an aliquot part of the potash solution is withdrawn and titrated. C. H. B.

Purification of Chloroform. By H. WERNER (*Arch. Pharm.* [3], **25**, 1113—1115).—The method of purifying chloroform published by the author in 1878 (Abstr., 1878, 821) affords a product found to be perfectly satisfactory for medicinal use during 10 years' experience, even if an isolated sample, may barely pass the phenolphthaleïn tests given by Vulpius (this vol., p. 634). J. T.

Geuther's Views on the Constitution of the Nitro-derivatives of the Adipic Hydrocarbons. By V. MEYER (*Annalen*, **244**, 222—224).—A reply to Götting's remarks on the constitution of nitroethane (this vol., p. 355).

Ethyl Ferrocyanide. By M. FREUND (*Ber.*, **21**, 931—936).—When a carefully cooled alcoholic solution of hydroferrocyanic acid is saturated with dry hydrogen chloride, a compound, $C_{18}H_{42}N_6O_6FeCl_2$, is obtained (compare Buff, *Annalen*, **91**, 253), which crystallises in white needles, decomposes into its constituents on exposure to the air, and when heated becomes dark-blue, and at a higher temperature glows, leaving a pseudomorph of iron oxide. Alcoholic ammonia converts it into the ammonium salt, $(NH_4)_4FeCy_6,2NH_4Cl$. Contrary to Buff's statement, ethyl ferrocyanide is not formed when it is dissolved in hot alcohol and treated with ether, since the product is hydroferrocyanic acid, and on this account the compound is to be regarded as probably analogous in constitution to the imido-ethers, and may be represented by the formula $H_4FeC_6(OEt)_6(NH)_6,2HCl$. The corresponding *methyl-*, *propyl-*, and *amyl-*derivatives were also prepared.

Ethyl ferrocyanide, Et_4FeCy_6, is obtained by boiling silver ferrocyanide with ethyl iodide for about an hour until the product begins to be coloured blue. It crystallises from chloroform by spontaneous evaporation in large, rhombic forms, decomposes at 212—214° with the formation of ethylcarbamine, and is readily soluble in water, alcohol, and chloroform, but insoluble in ether, light petroleum, and carbon bisulphide. In aqueous solution, it yields a deep-violet colour with ferric chloride, and a white precipitate with mercuric chloride. Concentrated sulphuric acid decomposes it with the formation of carbonic oxide and the sulphates of iron, ammonia, and ethylamine.

When finely powdered potassium ferricyanide, suspended in alcohol, is saturated with dry hydrogen chloride, a compound, $C_{18}H_{42}N_6O_6FeCl_3$ or $C_{18}H_{41}N_6O_6FeCl_2$, is obtained, which crystallises in needles, decomposes very readily, and in its other properties resembles the compound prepared from hydroferrocyanic acid. W. P. W.

Ethyl Platinocyanide. By M. FREUND (*Ber.*, **21**, 937—938).—The compound obtained by v. Than (*Annalen*, **107**, 315), and by him termed ethyl platinocyanide, most probably has not this composition but is analogous in constitution to the imido-ethers. For example, when heated on a water-bath it is converted into hydrogen platinocyanide, when decomposed with water it yields hydrogen platinocyanide and alcohol, and on treatment with alcoholic ammonia it is converted into ammonium platinocyanide (compare preceding Abstract).

W. P. W.

Formation of a Glycol in the Alcoholic Fermentation of Sugar. By HENNINGER and SANSON (*Compt. rend.*, **106**, 208—209).—Sugar was mixed with yeast, and after 15 days tartaric acid was added. When fermentation ceased, the product was fractionated and the portion boiling between 175° and 182° was refractionated. In this way, isobutylene glycol boiling at 178—179° was obtained, the yield amounting to 3·08 grams per kilo. of sugar. C. H. B.

Formose and Methylenitan. By O. LOEW (*J. pr. Chem.* [2], **37**, 203—206).—In this paper, the author contests the opinion advanced by Tollens (this vol., p. 438), that formose and methylenitan are identical. The reducing power of formose is nearly equal to that

of dextrose, it has a sweet taste, and if dried carefully, so as to prevent decomposition, gives on analysis numbers corresponding with the formula $C_6H_{12}O_6$. Methylenitan has, on the other hand, a bitter taste, a reducing power of only one-fifth to one-fourth of that of dextrose, does not yield an osazone, and is represented by the formula $C_6H_{10}O_5$.
G. T. M.

Alcoholic Fermentation of Galactose. By E. BOURQUELOT (*Compt. rend.*, **106**, 283—286).—Pure galactose is not fermented by either high or low beer yeast, but if the galactose is mixed with glucose and then with yeast it undergoes alcoholic fermentation. The limit of fermentation is the same whether the glucose and galactose are mixed in equal proportions, or the former is only one-thirtieth of the latter, but with the smaller proportion of glucose about thrice the time is required.

Levulose or maltose mixed with galactose and yeast have the same effect as glucose, and bring about the fermentation of the galactose.
C. H. B.

Compounds of Sugars with Aldehydes and Acetones. By H. SCHIFF (*Annalen*, **244**, 19—28).—The addition of a small quantity of aldehyde or acetone to a cold concentrated solution of glucose or cane-sugar in strong acetic acid, produces a gum-like deposit which adheres to the sides of the vessel. By washing the substance with glacial acetic acid, and afterwards treating it with absolute alcohol, it solidifies to a hygroscopic mass readily decomposed by water. These compounds contain sugar and aldehyde or acetone in equal molecular proportions. Dextrose forms compounds with benzaldehyde, salicaldehyde, cumaldehyde, furfuraldehyde, acetaldehyde, ethyl acetoacetate, and camphor, and cane-sugar combines with œnanthaldehyde, furfuraldehyde, and camphor. Milk-sugar does not form similar compounds.
W. C. W.

Bases formed by Alcoholic Fermentation. By E. C. MORIN (*Compt. rend.*, **106**, 360—363).—A quantity of crude unwashed fusel oil boiling at 130—135° was agitated with dilute hydrochloric acid, and the separated acid solution distilled until the last traces of alcohol were expelled. It was then made alkaline and again distilled, when the bases passed over with the first portions of the distillate. The bases were dried over potash and separated into three fractions, boiling respectively at 155—160°, 171—172°, and 185—190°. Similar products were obtained from both washed and unwashed fusel oils, but the yield was smaller in the case of the former.

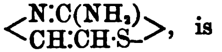
The base boiling at 171—172° has the composition of $C_7H_{10}N_2$. It is a mobile, colourless, highly refractive, almost neutral liquid with a strong disagreeable odour; sp. gr. = 0·9826 at 12°; vapour-density 4·16. When heated with hydrochloric acid, it is partially decomposed with formation of ammonium chloride, but no evidence as to its constitution is obtained. It combines with ethyl iodide, forming yellow needles which dissolve in water and alcohol but are insoluble in anhydrous ether. The *hydrochloride* crystallises in slender, white needles, soluble in water and ethyl alcohol, but only slightly soluble in ether. The platinochloride is crystalline and very soluble in water and alcohol, but only slightly soluble in ether, although it dissolves in a mixture of ether and alcohol. It decomposes when the aqueous or alcoholic solution is evaporated in a vacuum.

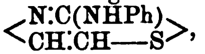
Mercury potassium iodide gives no precipitate in aqueous solutions, but after the addition of a small quantity of hydrochloric acid it yields a yellow, flocculent precipitate which rapidly changes to characteristic brilliant, slender needles.

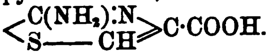
Pyridine and quinoline bases do not give this reaction. Mercuric chloride or phosphotungstic acid produces a flocculent, white precipitate; phosphomolybdic acid, a yellow precipitate. C. H. B.

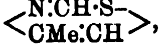
Bases produced by Alcoholic Fermentation. By TANRET (*Compt. rend.*, **106**, 418—419).—The base, $C_7H_{10}N_2$, obtained by Morin from the products of alcoholic fermentation (preceding Abstract) seems to be identical with the glucosine, $C_7H_{10}N_2$, obtained by the author by the action of ammonia on glucose (Abstr., 1885, 1048). C. H. B.

Amidothiazoles from Thiocarbamide and Halogenated Ketones and Aldehydes. By A. HANTZSCH and V. TRAUMANN (*Ber.*, **21**, 938—941).—The authors find that not only does the reaction between halogenated ketones and thiocarbamide-derivatives take place more readily than with ammonium thiocyanate (this vol., p. 256), but the yield also is almost quantitative, and the products consist not of substituted thiocarbamides as Pawlewski states (this vol., p. 473), but of thiazole-derivatives. Thus, the product of the action of chloracetone on thiocarbamide is not acetonylthiocarbamide but mesoamidomethylthiazole. The term thiazoline is proposed for amidothiazole.

Thiazoline,  $<\substack{N:C(NH_2)\\ CH:CH\cdot S-}>$, is prepared from dichlorether, and *phenylthiazoline* from bromacetophenone by the action of thiocarbamide. These strongly characterised bases resemble in their properties the bases of the aromatic series, and like these can be diazotised, forming diazothiazole salts, which react with aromatic amines and with phenols, yielding the corresponding amido- and hydroxy-azo-derivatives.

Mono-substituted thiocarbamides yield secondary thiazylamines by the action of halogenated ketones. *Phenylamidothiazole* or *thiazylaniline*,  $<\substack{N:C(NHPh)\\ CH:CH\text{——}S}>$, is obtained from phenylthiocarbamide and dichlorether.

The so-called sulphuvinuric acid, prepared by Nencki and Sieber (Abstr., 1882, 501) by the action of thiocarbamide on dibromopyruvic acid, is most probably amidothiazolecarboxylic acid,  $<\substack{C(NH_2):N\\ S\text{——}CH}>C\cdot COOH$. W. P. W.

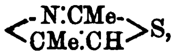
Methylthiazole. By A. HANTZSCH and L. ARAPIDES (*Ber.*, **21**, 941—942).—The authors have obtained the free thiazoles. *α-Methylthiazole*,  $<\substack{N:CH\cdot S-\\ CMe:CH}>$, is formed when the hydroxy-derivative (this vol., p. 256) is distilled with zinc-dust. It resembles α-picoline in every respect, particularly in odour and boiling point.

When the reaction-product of dichlorether and barium thiocyanate is distilled with zinc-dust, small quantities of a compound with a strong pyridine smell are obtained; this substance is most probably *thiazole*.

F. S. K.

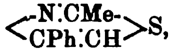
Synthesis of Thiazoles and Oxazoles. By A. HANTZSCH (*Ber.*, **21**, 942—946).—Thioamides condense with α-halogen-substituted ketones to form thiazoles.

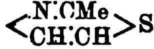
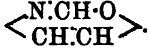
Thioacetamide and chloracetone yield *αα-dimethylthiazole*,



$$<\begin{array}{c}\text{N:CMe-}\\ \text{CMe:CH}\end{array}>\text{S},$$

a base which in smell, boiling point, &c., can scarcely be distinguished from αα-lutidine.

Phenylmethylthiazole,  $<\begin{array}{c}\text{N:CMe-}\\ \text{CPh:CH}\end{array}>\text{S}$, is formed by the condensation of thiacetamide with acetophenone bromide.

Methylthiazole,  $<\begin{array}{c}\text{N:CMe}\\ \text{CH:CH}\end{array}>\text{S}$, is produced, but only in small quantities, by the condensation of dichlorether with thioacetamide. *Oxazoles* are obtained by the condensation of α-halogen-ketones with amides; the compounds obtained by Lewy (this vol., p. 556) from acetophenone bromide and acetamide, and also the other compounds which he produced in a similar manner, are doubtless derivatives of oxazole,  $<\begin{array}{c}\text{N:CH·O}\\ \text{CH:CH}\end{array}>$.

Since the products obtained from amides are analogous to those produced from thiamides, it is probable that amides also exist in an unstable form, OH·CX:NH, in which they enter into the reaction. This conclusion is borne out by the fact that they only react at a higher temperature than do the thioamides.

Many derivatives of *selenazole* have also been prepared, and will be described later.

F. S. K.

Chloroformamide and its Use in Synthesis. By L. GATTERMANN (*Annalen*, **244**, 29—76).—The properties of chloroformamide and its preparation from carbonyl chloride and ammonium chloride have been previously described by the author and Schmidt (Abstr., 1887, 569).

Analogous compounds are obtained by the action of carbonyl chloride on methylamine and ethylamine hydrochlorides. NHMe·COCl melts at 90°, and boils at 93—94°. NHEt·COCl boils at 92—93°, and dissociates into hydrogen chloride and ethyl isocyanate.

Chloroformamide is decomposed by an excess of absolute methyl alcohol, yielding methyl carbamate, but if the methyl alcohol is slowly added to an excess of the chloroformamide, methyl allophanate is produced. Similar reactions are exhibited by other alcohols. *Octyl allophanate* melts at 155—156°, and *cetyl allophanate* at 70°. An ethereal solution of ethylene chlorhydrin yields *chlorethyl carbamate*, $NH_2{\cdot}COO{\cdot}C_2H_4Cl$. It is deposited from hot water in colourless, highly refractive plates, and melts at 115°. *Ethylene carbamate* (from glycol) is soluble in warm water, alcohol, and warm acetic acid. It melts at 147—149°. *Glyceryl carbamate*, $C_3H_5(O{\cdot}CONH_2)_3$, melts at 215°, *phenyl carbamate* at 143°, *α-naphthyl carbamate* at 158°, *β-naphthyl carbamate* at 187°, *orthophenylene carbamate* at 178°, the *meta*-compound at 194°, and the *para*-compound at 236°. Pyrogallol yields a carbamate, $C_6H_3(O{\cdot}CONH_2)_3$, melting at 178°. Salicaldehyde is converted by chloroformamide into "*disalicylaldehyde*," which is also the product of the action of acetic or benzoic chloride on the aldehyde. *Phenyl thioallophanate* melts at 218°.

The synthesis of several aromatic acids by the action of aluminium chloride and chloroformamide (or its homologues) on hydrocarbons diluted with carbon bisulphide, has already been described (*loc. cit.*). Similar results are obtained in the case of thio-compounds, thus: β-thiotolen yields an amide, melting at 119°, which is converted by saponification into methylthiophenic acid. Metathioxen yields an amide, $C_4SHMe_2{\cdot}CONH_2$, which crystallises in colourless needles, and melts at 115—116°. On hydrolysis, *dimethylthiophenoarboxylic acid*, $C_4SHMe_2{\cdot}COOH$ [$Me_2 : COOH = 2 : 4 : 5$], is obtained; this crystallises in needles, and melts at 171—172°. From trimethylthiophen, an amide, $C_4SMe_3{\cdot}CONH_2$, melting at 146—147°, and *trimethylthiophencarboxylic acid*, [$Me_3 : COOH = 2 : 3 : 4 : 5$], are obtained. The acid forms thick prisms, and melts at 207—208°.

In accomplishing the synthesis of aromatic acids, ethers may be used instead of hydrocarbons; thus, anisic acid can be prepared from anisoïl, and paraethoxybenzoic acid from phenetoïl. Orthocresyl methyl ether yields an amide, $OMe{\cdot}C_7H_{10}{\cdot}CONH_2$, from which the acid $OMe{\cdot}C_6H_3Me{\cdot}COOH$ [$MeO : COOH = 1 : 2 : 4$] is derived. The acid melts at 193°, the amide at 144°. Orthocresyl ethyl ether yields analogous results. The amide melts at 167°, and the acid at 199°. Paracresyl methyl ether yields an amide, [$Me : CONH_2 : OMe = 1 : 3 : 4$], which crystallises in colourless needles, melts at 163°, and yields methoxyparahomosalicylic acid on hydrolysis.

The amide derived from thymyl methyl ether melts at 149°, and is saponified with difficulty, yielding the acid $OMe{\cdot}C_{10}H_{12}{\cdot}COOH$, which has been described by Leuckart and Schmidt. Chloroformamide acts on methylene phenyl ether in presence of aluminium chloride, yielding the amide $C_2H_4(O{\cdot}C_6H_4{\cdot}CONH_2)_2$. This substance melts at 280° with decomposition. The amide from α-naphthyl methyl ether melts at 232°, and that from α-naphthyl ethyl ether melts at 244°. The latter, on hydrolysis, yields *ethoxynaphthoic acid*, $OEt{\cdot}C_{10}H_6{\cdot}COOH$. This forms colourless needles, and melts at 214°. The amide from β-naphthyl methyl ether melts at 186°, and that from β-naphthyl ethyl ether crystallises in large plates, and melts at 161°. Neither of these β-amides could be saponified. W. C. W.

Action of Aluminium Chloride on Acetic Chloride. By G. Gustavson (*J. pr. Chem.* [2], **37**, 108—110).—The substance obtained by Combes (Abstr., 1887, 127, 656) by the interaction of aluminium chloride (1 mol.) with acetic chloride (6 mols.) has really the constitution $Al_2Cl_4(O{\cdot}CCl_2{\cdot}CHAc_2)_2$, and on treatment with alcohol gives ethyl acetylacetoacetate, $CHAc_2{\cdot}COOEt$ (James, Trans., 1885, 1).

In all probability, the compound $Al_2Cl_4(O\cdot CCl_2\cdot CHAc_2)_2$ is formed by the direct addition of acetic chloride to the compound

$$Al_2Cl_4(O\cdot CCl\colon CHAc)_2,$$

which has been prepared by Winogradoff. G. T. M.

Ethereal Amidoacetates. By T. Curtius and F. Goebel (*J. pr. Chem.* [2], **37**, 150—181).—The hydrochlorides of ethereal salts of amidoacetic acid (glycocine) are produced when perfectly dry hydrogen chloride is passed into pure alcohol (half a litre) in which finely divided glycocine hydrochloride (100 grams) is suspended. The *methyl amidoacetate hydrochloride*, $NH_2\cdot CH_2\cdot COOMe,HCl$, forms large prisms melting at 175°. The platinochloride crystallises in orange-yellow plates, readily soluble in water and alcohol. *Ethyl amidoacetate hydrochloride*, $NH_2\cdot CH_2\cdot COOEt,HCl$, crystallises in colourless needles melting at 144°, and on careful heating sublimes unchanged. The platinochloride forms needles, readily dissolved by water and alcohol, and melting at 211—212°. Allyl amidoacetate hydrochloride does not crystallise well. It forms glistening scales melting somewhere between 170° and 180°. The amyl amidoacetate hydrochloride, $NH_2\cdot CH_2\cdot COOC_5H_{11},HCl$, forms an oily syrup. The copper salts, $(COOEt\cdot CH_2\cdot NH)_2Cu + 2H_2O$ and $(COOMe\cdot CH_2\cdot NH)_2Cu + H_2O$, are formed when the hydrochlorides are boiled with freshly precipitated hydrated copper oxide. Ethyl amidoacetate, when distilled with soda, gives normal propylamine, the hydrochloride of which melts at 157—158°; hence its constitution must be $NH_2\cdot CH_2\cdot COOEt$, and not $NHEt\cdot CH_2\cdot COOH$.

The free ethereal salts are best obtained by shaking their hydrochlorides with ether and finely divided silver oxide. They can be purified by distillation under reduced pressure. *Ethyl amidoacetate*, $NH_2\cdot CH_2\cdot COOEt$, is a colourless, transparent liquid boiling at 148—149° under a pressure of 748 mm., and at 65° under a pressure of 40 mm. It does not solidify at —20°. Vapour-density, 3·47; calculated, 3·57. It has strong basic properties, a characteristic odour resembling fresh cacao, and mixes with water, alcohol, ether, benzene, and chloroform. *Methyl amidoacetate*, $NH_2\cdot CH_2\cdot COOMe$, cannot be distilled at ordinary pressures without decomposition; under a pressure of 50 mm., it boils at 54°, and can be distilled without suffering change. In other respects, it greatly resembles the ethyl salt.

Glycocine anhydride, C_2H_3NO, is formed when ethyl amidoacetate is allowed to remain for some days with four times its own volume of water, or when the ether in aqueous solution is shaken with silver oxide. It crystallises in flat plates, and when quickly heated sublimes in beautiful, long needles, blackens at 245—260°, and seems to melt at 275°. Glycocine anhydride is neutral to litmus-paper, but forms compounds with acids, salts, and the heavy metals, and probably has the constitution $CH_2<\begin{matrix}NH\\CO\end{matrix}>$. The compounds it forms with silver, $NAgC_2H_2O$, and copper are described. It forms a hydrochloride which crystallises from alcohol in long needles melting at 129—130°, and on boiling with water is converted into glycocine hydrochloride melting at 180°. On distillation, ethyl amidoacetate leaves a residue, which, after boiling with charcoal and recrystallisation, has the formula $C_9H_{13}O_4N_5$. G. T. M.

Analogy between Alkyl-sulphonated Fatty Acids and Ketone Acids. By R. OTTO and W. OTTO (*Ber.*, **21**, 992—998; compare this vol., p. 360).—*Ethylsulphoneacetic acid*, $SO_2Et\cdot CH_2\cdot COOH$.—The ethyl salt of this acid (Claesson, this Journal, 1877, ii, 297) is a thickish, slightly yellowish oil which is quickly hydrolysed by concentrated potash. The free acid forms a thick, colourless, odourless syrup, which, on heating at 180—190°, yields carbonic anhydride and methylethylsulphone (Beckmann, Abstr., 1879, 37). The *sodium* salt is very readily soluble in water, and crystallises from boiling 90 per cent. alcohol in thin, nacreous leaves; it is only sparingly soluble in boiling absolute alcohol, and when heated to about 130°, it yields sodium carbonate and methylethylsulphone. When the acid is treated with bromine, carbonic anhydride and dibromomethylethylsulphone are produced; when treated with zinc and hydrochloric acid, it is reduced to ethyl mercaptan.

α-Ethylsulphonepropionic acid, $SO_2Et\cdot CHMe\cdot COOH$.—The ethyl salt is obtained by heating sodium ethylsulphinate with ethyl α-chloropropionate; it is a thick, yellowish oil of feeble ethereal odour, and is miscible with ether and alcohol in all proportions. The free acid is a thick, odourless, slightly yellow oil which is miscible with water and alcohol. It is decomposed into carbonic anhydride and diethylsulphone when heated to about 200°, or when heated with potash to about 150°. The *sodium* salt is readily soluble in water and alcohol.

β-Ethylsulphonepropionic acid, $SO_2Et\cdot CH_2\cdot CH_2\cdot COOH$, prepared by the action of sodium ethylsulphinate on β-iodopropionic acid, crystallises in small, shining leaves melting at 112°; it is very readily soluble in water, alcohol, and ether. The *sodium* salt is very readily soluble in water and alcohol. When the acid is heated to about 150° with a large excess of potash, it remains unchanged, but when the temperature is raised to 200° it is decomposed with formation of propionic acid and sulphur dioxide. When heated alone, the acid yields mercaptan, sulphur dioxide, and other products.

α-Phenylsulphonebutyric acid, $SO_2Ph\cdot CHEt\cdot COOH$, is obtained by the action of sodium benzenesulphinate on α-monobromobutyric acid; it crystallises in shining needles which melt at 123—124°, dissolves readily in ether and alcohol, but less readily in water. The *barium* salt is a gummy mass readily soluble in water, but insoluble in absolute alcohol. The *sodium* salt is amorphous.

When α-phenylsulphonebutyric acid is distilled, carbonic anhydride and propylphenylsulphone are produced; the latter compound crystallises from dilute alcohol in aggregates of nacreous leaves or scales which melt at 44°, dissolve readily in alcohol and benzene, but only sparingly in boiling water. Propylphenylsulphone is also formed when the acid is heated with an excess of potash at 100°. Bromine has no action on the aqueous solution of the acid.

From the above results, it follows that the fatty alkyl-sulphonic acids which contain alcohol radicles of the methane series, and are comparable with the β- and γ-ketone acids, obey the same laws as similar acids which contain aromatic alcohol radicles (this vol., p. 360); this is probably also true for similarly constituted fatty acids belonging to the α-series, $SO_2R\cdot COOH$. F. S. K.

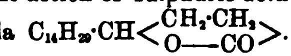
Occurrence of Lignoceric and Arachidic Acids in Earth-nut Oil. By P. Kreiling (*Ber.*, **21**, 880—881).—The author finds that lignoceric acid, first prepared by Hell and Hermann from beech-tar (Abstr., 1881, 249), occurs in earth-nut oil. He also confirms Gössmann's statement (*Annalen*, **89**, 1) that arachidic acid occurs in this oil.

Occurrence of Oleïc Acid in Earth-nut Oil. By L. Schön (*Ber.*, **21**, 878—879).—The author has examined specimens of earth-nut oil, both commercial and prepared by himself from the nuts, and finds that the only acid of the oleïc series contained therein is ordinary oleïc acid. This is contrary to the statements of Gössman and Scheven (*Annalen*, **94**, 230) and of Schröder (*ibid.*, **143**, 22) that hypogæic acid occurs in this oil.

The following formulæ are quoted for new oleates, no description of which are, however, given: $LiC_{18}H_{33}O_2$; $Pb(C_{18}H_{33}O_2)_2,2PbO$; $Mn(C_{18}H_{33}O_2)_2$; $Fe(C_{18}H_{33}O_2)_3$; $Al_2(C_{18}H_{33}O_2)_6$. A. J. G.

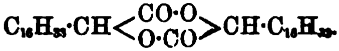
Action of Strong Sulphuric Acid on Oleïc Acid and Trioleïn. By A. C. Geitel (*J. pr. Chem.* [2], **37**, 53—90).—The author has investigated the behaviour of strong sulphuric acid with both oleïc acid and tri-oleïn. The reaction is an exceedingly indefinite one, neither the oleïc acid nor the tri-oleïn becoming completely saturated even in presence of a large excess of sulphuric acid. The chief product in the case of oleic acid is an acid ethereal salt, in that of tri-oleïn a normal ethereal salt. The extent to which combination had taken place was ascertained by titrating the products with solutions of potash and iodine of known strength.

When one molecule of sulphuric acid is mixed with one molecule of oleïc acid at low temperatures, about one-third of the oleïc acid is converted into *α-stearinsulphuric acid*, $C_{15}H_{31}\cdot CH_2\cdot CH(SO_4H)\cdot COOH$, which forms a brown viscid fluid readily dissolved by water, alcohol, and ether, but insoluble in dilute acids, and in solutions of Glauber's salt. The potassium salt, $C_{15}H_{31}\cdot CH_2\cdot CH(SO_4K)\cdot COOK$, is a bright-brown, greasy soap, soluble in water, alcohol, and ether. The sodium salt is likewise an oil. The barium salt, $C_{18}H_{34}SO_6Ba$, forms an amorphous, white powder, insoluble in water, but readily dissolved by alcohol and ether. On boiling with acetic acid, it gives the acid salt, $(COOH\cdot C_{17}H_{34}\cdot SO_4)_2Ba$. Three copper salts are described.

Another product of the action of sulphuric acid on oleïc acid is an *anhydride* of the formula  $C_{14}H_{29}\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ O\text{——}CO\end{matrix}>$. This crystallises in small, white scales, melting at 47—48°. The calcium and lead salts of the acid are described.

When α-stearinsulphuric acid is boiled with dilute acids, *α-hydroxy-stearic acid*, $C_{15}H_{31}\cdot CH_2\cdot CH(OH)\cdot COOH$, is formed; this is a crystalline solid, melting at 81—81·5°, and dissolves readily in alcohol and ether. The calcium, lead, and copper salts are described. The acid readily loses water, forming first the monobasic acid,

$$C_{16}H_{33}\cdot CH(COOH)\cdot O\cdot CO\cdot CH(OH)C_{16}H_{33},$$

and by further loss the anhydride,  $C_{16}H_{33}\cdot CH<\begin{smallmatrix}CO\cdot O\\ O\cdot CO\end{smallmatrix}>CH\cdot C_{16}H_{33}$.

It is an exceedingly difficult matter to isolate the products of the action of sulphuric acid on the tri-oleïn. When those substances are carefully brought together in the ratio of 3 mols. of the former to 1 mol. of the latter, the chief final product is a monobasic acid of the formula $C_{16}H_{33}\cdot CH(SO_4H)COO\cdot C_3H_5(O\cdot CO\cdot CH{:}CH\cdot C_{15}H_{31})\cdot O\cdot CO\cdot CH(OH)\cdot C_{16}H_{33}$. The barium and copper salts form oils which are readily decomposed by potash. G. T. M.

Constitution of Acetoacetic, Succinosuccinic, and Quinonehydrodicarboxylic Acids. By A. GEUTHER (*Annalen*, **244**, 190—221).—The author maintains that the acetoacetic and succinosuccinic acids are not ketonic acids, and he points out that the results obtained by Israel (Abstr., 1886, 334, and 1887, 915) and by Isbert (Abstr., 1886, 1009) are evidence in favour of the formula $CH_3\cdot C(OH){:}CH\cdot COOEt$ for ethyl acetoacetate.

The author criticises Ebert's experiments (Abstr., 1885, 1122) on the constitution of succinosuccinic acid, and complains that Baeyer has incorrectly represented his views on this subject (Abstr., 1886, 223 and 445). W. C. W.

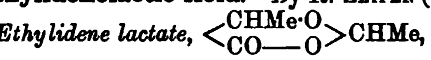
Methyl Acetocyanacetate. By A. HALLER and A. HELD (*Compt. rend.*, **106**, 210—213).—*Methyl acetocyanacetate*, $CN\cdot CHAc\cdot COOMe$, was obtained in the same way as the ethyl-derivative (Abstr., 1887, 799 and 1029), by the action of cyanogen chloride on a mixture, in molecular proportions, of methyl acetoacetate and sodium methoxide, dissolved in excess of methyl alcohol. It crystallises from ether in silky needles which melt at 46·5° and dissolve readily in ether or alcohol, but are insoluble in water.

The sodium-derivative, $C_6H_6NaNO_3$, is obtained by the action of sodium carbonate in alcoholic solution. It forms white, silky, anhydrous crystals soluble in water and alcohol. The calcium-derivative, prepared in a similar way, forms bulky, transparent, efflorescent crystals containing 6 mols. H_2O.

Methyl acetocyanacetate can also be prepared by mixing a solution of methyl sodiocyanacetate in methyl alcohol, with a solution of acetyl chloride in ether, and heating at 40—50° for some hours; the product is then treated with acidified water, submitted to fractionation in a vacuum, and the ethereal salt converted into its calcium-derivative.

If sodium ethoxide is used in place of the methoxide in the first method, the product is an uncrystallisable mixture of ethyl and methyl acetocyanacetates which cannot be separated by fractionation. It is evident that double decomposition takes place between the ethoxide and the methyl acetocyanacetate with formation of a mixture of methyl and ethyl salts. Purdie has observed a similar reaction in the case of the ethereal salts of fumaric, oxalic, and other acids (Trans., 1887, 627), and Peters in the case of methyl and ethyl acetoacetates (this vol., p. 254).

C. H. B.

Compounds of Ethylidenelactic Acid. By R. LEIPEN (*Monatsh. Chem.*, **9**, 45—51).—*Ethylidene lactate*,  $<\begin{matrix}\text{CHMe·O}\\ \text{CO——O}\end{matrix}>\text{CHMe}$, is obtained by heating acetaldehyde with an excess of lactic acid (previously partially converted by heating at above 150° into anhydride and lactide), for some hours at 120° to 170°. The product is distilled, and the portion boiling between 50° and 200° is treated with potassium carbonate, when the ether separates. It is a clear liquid of a slightly ethereal odour, boils at 150—151·5°, and dissolves in a large amount of water. Hot water decomposes it quickly into its constituents.

Lactanilide, $C_9H_{11}NO_2$, is prepared by heating lactic acid and aniline for six to seven hours on a sand-bath at such a temperature that water is given off, the liquid not being allowed to boil. The product is extracted with boiling water, and the filtered extract concentrated by evaporation. It crystallises in colourless plates, melting at 58°, readily soluble in alcohol, ether, and chloroform, but insoluble in light petroleum. Boiling dilute aqueous soda decomposes it.

Lactoparatoluide, $C_{10}H_{13}NO_2$, prepared in a manner similar to the anilide, crystallises in needles, melting at 102—103°, very sparingly soluble in cold water. The *orthotoluide* is purified by allowing the solution in benzene to evaporate slowly, when it separates as a white powder, melting at 72°. Both toluides resemble the anilide in solubility.

N. H. M.

Galactosecarboxylic Acid. By MAQUENNE (*Compt. rend.*, **106**, 286—288).—If a solution of galactose is mixed with hydrocyanic acid at the ordinary temperature, its rotatory power gradually disappears, and the liquid becomes brown. A concentrated solution deposits a yellowish, slightly soluble, crystalline precipitate, especially if the excess of hydrocyanic acid is expelled by a current of air. This precipitate is the amide of galactosecarboxylic acid, $C_7H_{15}NO_7$, and may be purified by crystallisation from boiling acetic acid, from which it separates in slender, yellowish, microscopic needles, slightly soluble in water, and almost insoluble in alcohol, but soluble in boiling acetic acid. It melts at 194° with partial decomposition.

When boiled with water, and especially with alkalis, the amide is readily decomposed with liberation of ammonia and formation of a salt of the acid. The formation of an amide shows that the action of hydrocyanic acid on galactose is not strictly analogous to its action on levulose.

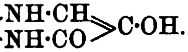
Galactosecarboxylic acid, $C_7H_{14}O_8$, is most readily prepared by decomposing its barium salt with sulphuric acid, and evaporating in a vacuum. It forms slender needles which melt at 145° and decompose at a higher temperature. It has a distinctly acid taste and reaction, and is soluble in water, but almost insoluble in absolute alcohol. Barium galactosecarboxylate, obtained by the action of barium hydroxide on the amide, forms long, slender, microscopic needles, which dissolve slowly in water, and are insoluble in alcohol. It is slightly dextrogyrate $[\alpha]_D = 5° 30'$.

This action of hydrocyanic acid shows that galactose has an aldehydic or ketonic function. C. H. B.

Action of Hydrocyanic Acid on Galactose. By H. KILIANI (*Ber.*, **21**, 915—919; compare preceding Abstract).—When finely powdered galactose (30 grams), moistened with water (6 c.c.), is treated with the calculated quantity of 50 per cent. hydrocyanic acid and a few drops of ammonia, and allowed to remain at the ordinary temperature in a perfectly closed flask, solution of the carbohydrate occurs and at the end of eight hours a rise in the temperature of the liquid takes place accompanied by the separation of the *amide* of galactosecarboxylic acid in small, white needles. The yield amounts to 40—50 per cent. of the weight of the galactose employed.

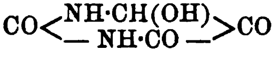
Galactosecarboxylic acid, $C_6H_{13}O_6\cdot COOH$, is prepared from the amide by digesting it with milk of lime at 100° to expel ammonia, decomposing the resulting basic calcium salt with oxalic acid, and evaporating the filtrate over sulphuric acid in a vacuum. It crystallises in slender needles, and melts at 145° with the loss of 2 mols. H_2O and the formation of an amorphous *anhydride;* a similar decomposition also occurs when the aqueous solution of the acid is boiled for some time. The *potassium* salt, $2C_6H_{13}O_6\cdot COOK + H_2O$, crystallises in colourless prisms or needles, and fuses at 110° with the loss of its water of crystallisation; the *calcium* salt was also prepared. On reduction with concentrated hydriodic acid and amorphous phosphorus for $1\frac{1}{2}$ hours in a reflux apparatus, the acid is converted into the lactone of normal γ-hydroxyheptylic acid (b. p. = 231°), and a very small quantity of normal heptylic acid, consequently galactosecarboxylic acid, like dextrosecarboxylic acid, must be regarded as a normal hexahydroxyheptylic acid. W. P. W.

Synthetical Experiments in the Uric Acid Series. By R. BEHREND and O. ROOSEN (*Ber.*, **21**, 999—1001).—Further experiments have shown that one of the products obtained by the reduction of nitrouracil (Behrend, *Annalen*, **229**, 39), is the ureïd of an α-β-dihydroxyacrylic acid or *isobarbituric acid*,



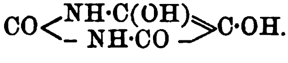
$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CH}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{C\cdot OH}$.

Hydroxylamine does not act on this compound, but when it is boiled with acetic anhydride, an acetyl-derivative is formed which crystallises from hot water in the form of sparingly soluble, colourless, concentrically grouped prisms. When isobarbituric acid is treated with bromine-water, it yields an acid which has the same composition as dialuric acid. This substance crystallises in solid prisms with 2 mols. H_2O, the first of which passes off at 100°, the second at 140—150°, apparently with slight decomposition. It differs from ordinary dialuric acid in crystalline form, water of crystallisation, and in its ready solubility in water as well as in its stability towards oxidising agents, it may therefore be termed *isodialuric acid*, and its formula is probably either



$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CH(OH)}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{CO}$$

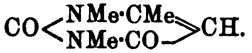
or



$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C(OH)}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{C\cdot OH}.$$

This acid is also formed by the action of bromine-water on amido-uracil and hydroxyxanthine. It is readily acted on by acetic anhydride. When heated with carbamide and concentrated sulphuric acid, a white, crystalline powder is obtained, the analysis of which agreed with that of uric acid. The compound is an acid, decomposes carbonates and gives the murexide reaction; it reduces Fehling's solution, and a dilute solution in sodium carbonate blackens paper moistened with silver nitrate. It crystallises from hot water in the right-angled plates which are characteristic of uric acid. The solubility in water at 18° was found to be 1 : 9000. The *sodium* salt, $C_5H_3N_4O_3Na,\frac{1}{2}H_2O$, crystallises in microscopic needles. The *barium* salt, $(C_5H_3N_4O_3)_2Ba,2H_2O$, is amorphous. F. S. K.

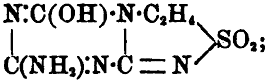
Trimethyluracil. By M. HAGEN (*Annalen*, **244**, 1—19).—The preparation of trimethyluracil by the action of methyl iodide on the potassium salt of methyluracil at 150°, has been described by Behrend (Abstr., 1886, 339). The excess of methyl iodide is removed from the crude product by distillation, and the residue is dissolved in water. The solution is agitated with chloroform, and sodium carbonate is added to the chloroform extract to remove free iodine. The residue which is left after distilling off the chloroform is treated with ether; the trimethyluracil slowly dissolves leaving a small residue of methyluracil dihydride.

Trimethyluracil crystallises in rhombic plates and melts at 109°. It does not form salts with acids or with bases. It is decomposed by barium hydroxide at 200°, yielding methylamine, and carbonic and acetic acids. Its constitution is probably represented by the formula  $CO<\begin{matrix}NMe\cdot CMe\\NMe\cdot CO\end{matrix}>CH$. Benzyl chloride acts on the potassium salt of methyl uracil, forming *benzylmethyluracil*, a crystalline compound melting at 232—233°.

Dry bromine or a solution of bromine in carbon bisulphide acts on dry trimethyluracil, forming a compound of the composition $C_4H_9NO_4Br_2$. *Dibromhydroxytrimethyluracil* is obtained as a white powder when bromine is added to an aqueous solution of trimethyluracil. It is deposited from a hot aqueous solution in rhombic plates, and melts at 163° with decomposition. It is decomposed by prolonged boiling with alcohol, yielding bromotrimethyluracil. This substance melts at 126°.

Dichlorhydroxytrimethyluracil melts with decomposition at 143—144°. It is converted into *chlorotrimethyluracil* by the action of stannous chloride.

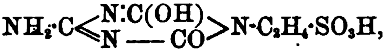
Amidotrimethyluracil is formed by acting on bromotrimethyluracil with strong ammonia at 140°. It melts at 166—167°, is soluble in water, and forms deliquescent salts. The hydrochloride interacts with an excess of potassium cyanate, forming *trimethylhydroxyxanthine* in small quantities; this crystallises in microscopic prisms.
W. C. W.

Cyanuric Derivatives of Taurine. By B. RATHKE (*Ber.*, **21**, 874—877).—When a solution of the hydrochloride of ethylenethiammeline (Abstr., 1887, 650) is treated with chlorine, a nearly insoluble compound separates in silvery plates; this seems to be an *inner* *anhydride* of *taurammeline* of the formula 

$$\begin{array}{l} N{:}C(OH)\cdot N\cdot C_2H_4 \\ | \qquad\qquad\qquad | \\ C(NH_2){:}N\cdot C = N \end{array} \Big> SO_2;$$

it dissolves in alkalis, presumably with conversion into the sulphonic acid, but is reprecipitated on addition of acids; with silver nitrate, it gives a white precipitate sparingly soluble in ammonia.

Taurodiammeline, $C_{10}H_{15}N_9S_2O_8$, is formed at the same time as the above compound, but is formed alone when the ethylenethiammeline is oxidised with nitric acid. It forms slender, transparent prisms, sparingly soluble in cold water; when heated, it begins to turn brown at 270°, but is still not melted at 290°. It has very marked acid characters; the salts with the alkalis and alkaline earths are readily soluble.

Taurammelide,  $NH_2\cdot C{<}\genfrac{}{}{0pt}{}{N{:}C(OH)}{N \text{---} CO}{>}N\cdot C_2H_4\cdot SO_3H$, is obtained on boiling the preceding compound with baryta-water; it forms sparingly soluble crystals, and melts at 265—270° with decomposition.

A. J. G.

Vapour-density of Aluminium Methide. By E. LOUISE and L. ROUX (*Compt. rend.*, **106**, 602—603).—The aluminium methide was prepared by the action of mercuric methide on excess of aluminium, and was redistilled over aluminium in pure and dry nitrogen. It is a colourless mobile liquid which boils at 140°, and is much less stable than aluminium ethide. The vapour-density was determined by Meyer's method at different temperatures.

Temperature	182°	216°	310°	340°	440°
Vapour-density	5·1	4·75	4·6	2·4	1·8

At 50° above the boiling point, the vapour-density agrees with the formula Al_2Me_6, but as the temperature rises, the compound gradually decomposes until at 440° the vapour-density is only 1·8. The products of decomposition are metallic aluminium and gaseous paraffins and olefines.

C. H. B.

2 : 5 Dibromocymene. By A. CLAUS (*J. pr. Chem.* [2], **37**, 14—27; see Abstr., 1880, 632; *Ber.*, **13**, 905, 972).—By direct bromination of paracymene, only one dibromoparacymene,

$$C_6H_2MePrBr_2 \; [Me : Pr : Br_2 = 1 : 4 : 2 : 5],$$

is obtained, which when nitrated with a mixture of nitric and sulphuric acids furnishes three nitro-derivatives, melting at 149°, 142°, and 89° respectively. The product melting at 149° has the formula—

$$C_6PrMe(NO_2)_2Br_2 \;\; [(NO_2)_2 = 3 : 6],$$

crystallises from alcohol in colourless needles, and is characterised by great stability. It is only imperfectly decomposed by heating with fuming nitric acid in sealed tubes at 280°, and is scarcely attacked by long-continued boiling with aqueous or alcoholic potash. The compound melting at 142° crystallises from ordinary solvents in yellow needles or prisms, and sublimes in small scales. It is a *dibromodinitrotoluene*, $C_6HMe(NO_2)_2Br_2 \, [Me : Br_2 : (NO_2)_2 = 1:2:5:4:6]$, and is readily attacked by potash. With aniline, it readily forms the compound $NHPh\cdot C_6HMeBr(NO_2)_2$, crystallising in glistening orange-red needles, melting at 116°. The third product melting at 89° is only formed in small quantity, but is practically the sole product of nitrating dibromocymene with fuming nitric acid at 100°. It is a dibromonitrotoluene, $C_6H_2Br_2Me{\cdot}NO_2$ [$Me : Br_2 : NO_2 = 1 : 2 : 5 : 4$], and can be readily further nitrated with formation of the compound above described melting at 142°. It is very soluble in petroleum and alcohol, from which it crystallises in long, colourless needles, and is identical with the substance described by Nevile and Winther (Trans., 1880, 429); and furnishes by reduction first a dibromotoluidine (m. p. 83—85°) and finally toluidine. The formation of dibromodinitrotoluene (m. p. 142°) by nitration of paracymene is remarkable, the propyl-group being oxidised and then replaced by a nitro-group.

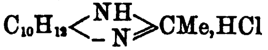
When dibromocymene is heated in sealed tubes for eight hours at 180° with 20 times its weight of nitric acid of sp. gr. 1·12, it is converted into dibromoterephthalic acid, which on treatment with phosphorus pentachloride yields a chloride—

$$C_6H_2Br_2(COCl)_2 \; [(COCl)_2 : Br_2 = 1 : 4 : 2 : 5],$$

readily soluble in carbon bisulphide and chloroform, and crystallising from ether in prisms melting at 80—81°. The corresponding amide, $C_6H_2Br_2(CONH_2)_2$, is insoluble in alcohol, ether, chloroform, and light petroleum, but dissolves sparingly in carbon bisulphide, from which it crystallises in fine needles; these carbonise at 300° without previously melting. By gentle oxidation, dibromocymene yields a monobasic acid of the formula $C_{10}H_{10}Br_2O_2$. The sodium salt forms beautiful colourless needles. The ammonium salt is only slightly soluble in water, and melts at 172°. The calcium salt crystallises in stellate groups of needles with 4 mols. of water, whilst the silver salt separates from a hot aqueous solution in needles containing 3 mols. H_2O. This acid is either dibromocumic acid, $C_6H_2PrBr_2{\cdot}COOH$ [$COOH : Pr : Br_2 = 1 : 4 : 3 : 6$], or dibromotolylpropionic acid, $C_6H_2Br_2Me{\cdot}C_2H_4{\cdot}COOH$. The author gives reasons in favour of its being the latter.

G. T. M.

Derivatives of 1 : 2 : 3 : 4 Tetramethylbenzene (Prehnitene). By A. Töhl (*Ber.*, **21**, 904—908).—Prehnitene combines with picric acid to form a fairly stable compound, which crystallises from alcohol in yellow needles and melts at 92—95°.

Nitroprehnitene, $C_{10}H_{13}{\cdot}NO_2$, is obtained when a thin layer of prehnitene is allowed to remain in contact with ordinary nitric acid for three to four days, and is purified by distillation with steam. It crystallises in stellate groups of flat needles, melts at 61°, boils with partial decomposition at 295° (thermometer in vapour), and is readily soluble in ether, alcohol, light petroleum, and acetic acid. On reduction with iron and acetic acid, it yields *prehnidine*, $C_{10}H_{13}{\cdot}NH_2$. This crystallises in large, lustrous, colourless scales, melts at 70°, is readily soluble in alcohol, ether, and light petroleum, and is volatile with steam. The *hydrochloride*, $C_{10}H_{13}NH_2,HCl$, crystallises from water in tufts of very long, colourless needles; the *sulphate*, $(C_{10}H_{13}NH_2)_2,H_2SO_4$, crystallises in large scales, and is sparingly soluble in cold water; the *nitrate* crystallises from water in six-cornered prisms. *Acetoprehnidine*, $C_{10}H_{13}{\cdot}NHAc$, crystallises from dilute alcohol in colourless needles, melts at 172°, is readily soluble in alcohol, and on treatment with ordinary nitric acid yields the *nitro*-derivative, $NO_2\cdot C_{10}H_{12}\cdot NHAc$. This compound can also be obtained by the action of acetic chloride on nitroprehnidine, and crystallises from dilute alcohol in hair-like, branching needles, melting at 225°. When reduced with tin and hydrochloric acid, it is converted into *ethenylprehnityleneamidine hydrochloride*,  $C_{10}H_{12}{<}\begin{matrix}NH\\ -N\end{matrix}{\gg}CMe,HCl + 2H_2O$, which crystallises in slender, colourless needles, and is readily soluble in water; the base is flocculent and contains 2 mols. H_2O.

Nitroprehnidine, $NO_2\cdot C_{10}H_{12}\cdot NH_2$, is prepared by the reduction of dinitroprehnitene (Abstr., 1886, 694) with alcoholic ammonium sulphide. It crystallises in lustrous, red needles, melts at 131°, and is soluble in alcohol and concentrated hydrochloric acid. On reduction, it yields *prehnitylenediamine*, $C_{10}H_{12}(NH_2)_2$, which crystallises from water in large, lustrous scales, from alcohol in long, colourless needles, melts at 140°, is sparingly soluble in ether and light petroleum, and gives the reactions characteristic of an orthodiamine. The *hydrochloride*, $C_{10}H_{12}(NH_2)_2,2HCl + H_2O$, crystallises in large, lustrous scales, and in dilute aqueous solution is coloured dark-red by ferric chloride and by potassium chromate.

Prehnitol, $C_{10}H_{13}\cdot OH$, obtained by fusing sodium prehnitenesulphonate with potassium hydroxide, crystallises from light petroleum in very long, colourless, silky needles, melts at 86—87°, boils at 266° (thermometer in vapour), and is very readily soluble in alcohol and ether. It is not coloured by ferric chloride. The *acetyl*-derivative, $C_{10}H_{13}\cdot OAc$, crystallises in large, well-formed prisms, and melts at 56—57°; the *bromo*-derivative, $C_{10}H_{12}Br\cdot OH$, crystallises in long, slender needles, and melts at 151°.

When oxidised with a dilute aqueous solution of permanganate at 100°, prehnitene is first converted into prehnitylic acid (*loc. cit.*), and finally yields prehnitic acid; a *potassium* salt of the latter,

$$C_6H_2(COOH)_3\cdot COOK + H_2O,$$

was obtained by treating the oxidation-product, after filtration, with acetic acid and lead acetate, decomposing the lead salt with hydrogen sulphide, and evaporating the filtrate; it crystallises in large aggregates.
W. P. W.

Bromodichlorophenol and Dibromodichlorobenzene. By L. Garzino (*Chem. Centr.*, 1887, 1546—1547; from *Rend. Acc. Lincei* [4], 3, 202—209).—*Bromometadichlorophenol*, $C_6H_2BrCl_2\cdot OH$ [? OH : Cl₂ : Br = 1 : 2 : 4 : 6], is obtained by adding the calculated quantity of bromine to a cooled solution of dichlorophenol (15 grams) in glacial acetic acid (10 grams). The separation of the product causes the mass to become semisolid. It is exposed to the air until the small excess of bromine has volatilised, then washed with plenty of water, dried, distilled in a vacuum, and finally sublimed. The pure product forms white needles, melting at 68°, and boiling with decomposition at 268°. Under a pressure of 200 mm., it distils unchanged at 220°. It sublimes moderately well at 130—140°. It is readily soluble in benzene, ether, and chloroform, also in concentrated acetic acid and alcohol, but is nearly insoluble in water. It is carried over with water vapour. Ferric chloride produces a light-blue colour in an alcoholic solution, but no colour in watery solution. It has hardly any smell and very little caustic action. No isomeride seems to be formed. Ammonium, sodium, potassium, barium, and silver salts, as well as the benzoate (m. p 67·5°) and phthalate (m. p. 216—217°), were prepared.

For the preparation of *dibromodichlorobenzene*, $C_6H_2Br_2Cl_2$ [? = 1 : 6 : 2 : 4], a mixture of 20 grams of the above bromodichlorophenol, and 45 grams of phosphorus pentabromide was slowly distilled. The part distilling between 200° and 350° was heated with a 25 per cent. solution of potash, dried, and repeatedly crystallised from a mixture of light petroleum (b. p. 30—80°).

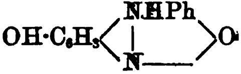
The pure product forms needles melting at 67—68°, very easily soluble in ether, light petroleum, and benzene. These crystals can be moderately easily sublimed. Besides this, another product is formed in small quantity, melting at 190·5—192°; this dissolves easily in ether and light petroleum, separates from benzene in small needles, and contains both chlorine and bromine. J. P. L.

Compounds of Phenoxides with Cuprous and Mercurous Chlorides. By A. G. POUCHET (*Compt. rend.*, **106**, 276—277).—A solution of phenol in sodium hydroxide when mixed with mercuric chloride yields a white precipitate of the composition $(C_6H_5O)_2Hg,Hg_2Cl_2 + 4H_2O$. β-Naphthol and α-anthrol yield respectively the compounds $(C_{10}H_7O)_2Hg,Hg_2Cl_2 + 4H_2O$ and $(C_{14}H_9O)_2Hg,Hg_2Cl_2 + 4H_2O$.

Strictly analogous compounds of cuprous chloride are obtained in precisely the same way. C. H. B.

Action of Aniline on Epichlorhydrin. By A. FAUCONNIER (*Compt. rend.*, **106**, 605—607).—Aniline (3 mols.) was heated at 140° and gradually mixed with epichlorhydrin (1 mol.). If the two liquids are first mixed and then heated, the reaction becomes explosively violent below 100°. The product is a brownish oil, which is dissolved in hydrochloric acid and reprecipitated by ammonia to remove aniline. The base is dissolved in ether, washed with water, then extracted with dilute hydrochloric acid, and the solution concentrated to a syrup, which gradually crystallises. It is purified by recrystallisation from alcohol. The hydrochloride thus obtained, $C_{15}H_{20}N_2Cl_2O$, forms colourless needles, very soluble in water, and somewhat soluble in alcohol, especially on boiling, but insoluble in ether. They become brown at 180°, soften at 196°, and melt with decomposition at 201—202°. The base is obtained by treating the hydrochloride with alkaline hydroxides, carbonates, or hydrogen carbonates, or even with sodium acetate, and forms a colourless, non-crystallisable oil, soluble in alcohol or ether, but insoluble in water. It seems to be isomeric with the dianilinehydrin obtained by Claus by the action of aniline on glycerol dichlorhydrin. The author proposes to call it *dianilglycerol*, and ascribes to it the constitution $NHPh{\cdot}CH_2{\cdot}CH(NHPh){\cdot}CH_2{\cdot}OH$. It gives the general reactions for alkaloïds, and reduces auric chloride and potassium ferricyanide in the cold. It gives a precipitate with mercuric chloride only in presence of sodium carbonate. The platinochloride forms pale-yellow lamellæ. Picric acid produces an amorphous, yellow precipitate soluble in acids; bromine-water or sodium hypochlorite, a dull green precipitate; potassium dichromate an intense brown coloration; potassium permanganate a very intense violet coloration. C. H. B.

Metahydroxyparanitrosodiphenylamine. By L. KOHLER (*Ber.*, **21**, 908—910).—*Metahydroxydiphenylnitrosamine*, $C_{12}H_{10}N_2O_2$, is obtained by dissolving hydroxydiphenylamine in alcohol, and adding the calculated quantities of dilute sulphuric acid and of an aqueous solution of sodium nitrite to the well-cooled solution. It crystallises in slender, yellow needles, melts with decomposition at 115°, and is readily soluble in ether, alcohol, and acetic acid, soluble in benzene and light petroleum. When it is dissolved in a mixture of 2 parts by weight of absolute alcohol and 7 parts of ether, and heated in the cold with 1 part of alcoholic hydrogen chloride, brown scales of a hydrochloride separate, from which *metahydroxyparanitrosodiphenylamine*,



$OH\cdot C_6H_3\langle NHPh \mid N \rangle O$ [NHPh : OH : N = 1 : 3 : 4], can be obtained by suspending them in water, adding a slight excess of aqueous soda, and precipitating the filtrate with carbonic anhydride. It crystallises from benzene in beautiful, red needles, and is soluble in acetone, benzene, and alcohol, sparingly soluble in ether, and very sparingly soluble in light petroleum. Ammonia and aqueous soda dissolve it readily, and its solution in concentrated sulphuric acid is coloured red. On reduction with tin and hydrochloric acid at the ordinary temperature, it yields *metahydroxyparamidodiphenylamine*, $C_{12}H_{12}N_2O$, which crystallises in pale bluish scales, melts at 135°, and is readily soluble in alcohol, chloroform, and acetone, soluble in benzene and ether, and very sparingly soluble in light petroleum.

Hydroxyazophenine, $C_{30}H_{24}N_4O$, is formed by heating metahydroxyparanitrosodiphenylamine with aniline and aniline hydrochloride at 100° for three hours. It crystallises from toluene in brown needles, melts at 197°, is insoluble in aqueous, but soluble in alcoholic potash and soda, and dissolves in concentrated sulphuric acid with a reddish-brown colour. W. P. W.

Condensation of Chloral Hydrate with Secondary Aromatic Amines. By P. BOESSNECK (*Ber.*, **21**, 782—783).—With aniline, chloral hydrate yields trichlorethylidenediphenylamine, with elimination of water (Wallach, this Journal, 1872, 611; Cech, *ibid.*, 1876, ii, 66), whilst tertiary amines undergo the aldol-condensation with chloral hydrate (Boessneck, Abstr., 1883, 976; 1884, 458. Knöfler and Boessneck, this vol., p. 267); the reaction with secondary amines is now shown to be similar to that of the tertiary compounds.

Methylamidophenylhydroxytrichlorethane, $CCl_3\cdot CH(OH)\cdot C_6H_4\cdot NHMe$, is obtained by mixing chloral hydrate and methylaniline in molecular proportion, moderating the violent reaction by cooling, and afterwards allowing the mixture to remain at about 40—50° for

24 hours; it is then supersaturated with ammonia, distilled with steam to remove unaltered methylaniline, and the hydrochloride precipitated by addition of concentrated hydrochloric acid; after washing with alcohol and recrystallising from hot water, this is decomposed by ammonia. It is crystalline, and melts with decomposition at 112°. The *hydrochloride* forms thick prisms, sparingly soluble in cold water. The *nitroso*-compound, $CCl_3\cdot CH(OH)\cdot C_6H_4\cdot NMe\cdot NO$, prepared by the action of sodium nitrite on the hydrochloride, crystallises in needles, melts at 117—118°, begins to decompose at 140°, and is soluble in alcohol, acetic acid, and ether.

Ethylamidophenylhydroxytrichlorethane, $CCl_3\cdot CH(OH)\cdot C_6H_4\cdot NHEt$, prepared in a manner similar to the methyl compound, is crystalline, and melts at 98°. The *hydrochloride* forms stellate group of needles, the *nitroso*-compound melts at 138°. A. J. G.

Reaction between Metaphenylenediamine and Carbon Bisulphide. By P. Gucci (*Chem. Centr.*, 1887, 1547; from *Atti Soc. Toscano Sc. Nat.*, **5**, 291—293).—*Thiocarbonylmetaphenylenediamine thiocarbonate* separates out in crystals after heating metaphenylenediamine and carbon bisulphide in sealed tubes for six hours with alcohol at 50—55°. After six hours' heating at 100°, a small quantity of a golden-yellow compound is formed in addition to the above. A further six hours' heating at 150° results in the latter substance alone being formed. The crystals are monoclinic, and do not give off hydrogen sulphide when boiled with alcohol. This compound is insoluble in water, ether, benzene, carbon bisulphide, and chloroform, and only sparingly soluble in ethyl and amyl alcohols.

At 280°, it remains unchanged, turns brown at 300°, and decomposes at a higher temperature. The author regards the compound as *sulphocarbonylmetapheneylenediamine*, $C_6H_4{:}N_2H_2{:}CS$. J. P. L.

Diazo-compounds. By P. Griess (*Ber.*, **21**, 978—984).—The author has experimented on the behaviour of the three isomeric diazobenzoic acids towards methyl and ethyl alcohols and phenol. In the first two cases, 1 part of the acid, in the form of sulphate, was heated with 10 parts of the alcohol until the evolution of nitrogen ceased; in the experiments with phenol, 1 part of the sulphate was added to 2 to 3 parts of phenol, heated to its melting point, and the well-mixed mass warmed gently until the commencement of the reaction, which is always very energetic.

By methyl alcohol, metadiazobenzoic acid is completely converted into methylmetahydroxybenzoic acid. The product crystallises in white needles, which are very sparingly soluble in cold water, and melt at 107°.

Paradiazobenzoic acid and methyl alcohol yield methylparahydroxybenzoic acid, which melts at 183—184°, whilst orthodiazobenzoic acid yields only benzoic acid.

With ethyl alcohol, metadiazobenzoic acid yields a mixture of benzoic and ethylmetahydroxybenzoic acid. The products can be easily separated as the latter is almost insoluble in water; it forms white, crooked needles, melting at 137°.

Paradiazobenzoic acid with methyl alcohol yields benzoic and ethylparahydroxybenzoic acids, which can be separated as in the preceding case; the latter acid melts at 107°. Orthodiazobenzoic acid is completely converted into benzoic acid.

With phenol, metadiazobenzoic acid yields *metaphenoxybenzoic acid;* this crystallises from dilute alcohol in long, white needles, melting at 145°. It is almost insoluble in boiling water, but dissolves readily in alcohol and ether; it can be distilled in small quantities without decomposition. The barium salt, $(OPh{\cdot}C_6H_4{\cdot}COO)_2Ba + 3\frac{1}{2}H_2O$, crystallises in small, white, ill-defined leaves.

Paradiazobenzoic acid and phenol give paraphenoxybenzoic acid, which has already been described by Klepl (Abstr., 1884, 446). Orthodiazobenzoic acid yields hydroxydiphenylene ketone, orthophenoxybenzoic acid, and a new compound, which crystallises in white, shining needles, melting at 205°, and is tolerably readily soluble in hot water. This product seems to be isomeric with orthophenoxybenzoic acid.

Hydroxydiphenylene ketone melts at 96°, not 91° as stated by Richter (Abstr., 1884, 325).

Orthophenoxybenzoic acid is identical with the phenylsalicylic acid obtained by Graebe (this vol., p. 477).

The sulphate of orthotetrazodiphenic acid, $C_{12}H_6(N_2SO_4H)_2(COOH)_2$, a compound which is obtained from the sulphate of orthodiamidodiphenic acid by treating it with nitrous acid, when warmed with ethyl alcohol, yields aldehyde, sulphuric acid, nitrogen, and a new *diphenic acid*, $C_{12}H_6(COOH)_2$ [$(COOH)_2 = 3 : 3'$]. The latter is precipitated from its dilute ammoniacal solution in white, microscopic needles, and crystallises from boiling alcohol in small leaves. It is almost totally insoluble in cold water, and dissolves only sparingly in hot water, but more readily in hot alcohol, ether, and chloroform. The *barium salt* is tolerably readily soluble in water, from which it crystallises only slowly in nodular masses, having the formula $C_{14}H_8O_4Ba + 3\frac{1}{2}H_2O$. If the aqueous solution is evaporated down by boiling, the salt separates in needles which only contain 1½ mol. H_2O. When the salt is subjected to dry distillation, it yields diphenyl (m. p. 70°) and barium carbonate. F. S. K.

Action of Potassium Ferrocyanide on Diazobenzene Nitrate. By M. Locher (*Ber.*, **21**, 911—913).—The yellow, crystalline compound (m. p. = 150°) obtained, together with azobenzene and an oil, by Griess by the action of a cold saturated solution of potassium ferrocyanide on diazobenzene nitrate (this Journal, 1876, i, 932), when heated with aniline hydrochloride and aniline at 160°, yields an induline which is insoluble in alcohol. When reduced by the action of hot hydrochloric acid and tin, or by heating with concentrated hydriodic acid and amorphous phosphorus at 120—130°, Griess' compound is converted into aniline and paramidodiphenyl, and must therefore be regarded as benzeneazodiphenyl, $Ph{\cdot}N_2{\cdot}C_6H_4Ph$. The *hydrazo*-derivative, $C_{18}H_{16}N_2$, obtained by treating its solution in absolute alcohol first with ammonia and then with hydrogen sulphide, crystallises in needles or thin scales, melts at 127°, and is readily converted into benzeneazodiphenyl by exposure to the air and by distillation. Concentrated sulphuric acid dissolves it with a dark-red colour, which afterwards changes to green. When the hydrazo-derivative is boiled with acetic anhydride, the *acetyl*-derivative, $C_{18}H_{14}N_2Ac_2$, is formed; this crystallises in small, white needles, decomposes partially at 190° with the production of a yellow colour, and melts at 202—203°.

Under like conditions, potassium ferrocyanide reacts with diazo-α-naphthylamine (? naphthalene), and two compounds are obtained; one of these crystallises in dark-red, spherical aggregates, melts at about 200°, and seems to be azonaphthalene. W. P. W.

Hydrazones. By E. Fischer (*Ber.*, **21**, 984—988).—The name hydrazone is proposed for the compounds of hydrazine with aldehydes and ketones, and the term *osazone* for those compounds containing two neighbouring hydrazone-groups. Other compounds containing two hydrazone-groups may be named *dihydrazones*. Since phenylhydrazine is almost the only reagent employed, the word "phenyl" may usually be dispensed with.

The author gives the following reasons why the hydrazones must be considered as isomeric and not identical with the azo-compounds:—(1) Hydrazone-formation takes place equally well with a primary or with a secondary hydrazine, but in the latter case the formation of an azo-compound is excluded. (2) Most hydrazones regenerate the hydrazine bases when boiled with acids; only in isolated cases are indoles formed instead. (3) The hydrazone of acetaldehyde is isomeric with benzeneazoethane. Of the two formulæ for hydrazones, $R{\cdot}NH{\cdot}N{:}C{=}$ and $<^{NH}_{NR}>C{=}$, the author considers the former as the most probable, and that the osazones are similarly constituted. In taking the melting point of a hydrazone, it should be borne in mind that many of them melt with decomposition, and constant melting points can only be obtained by raising the temperature as quickly as possible. F. S. K.

Compounds of Phenylhydrazine with Sugars. By E. Fischer (*Ber.*, **21**, 988—991).—The conversion of any known sugar into the crystalline and sparingly soluble osazone is the best method for recognising the former, or for isolating new compounds belonging to this class of substances.

By this method it was found that *phlorose*, the sugar obtained from phloridzin by Hesse (Abstr., 1878, 851), is identical with dextrose. *Crocose*, a sugar prepared from saffron, also consists of dextrose, but it was not proved whether any other sugar is present or not. Formose, the product obtained from formaldehyde and calcium hydrate (Butlerow, *Compt. rend.*, **53**, 145; Loew, Abstr., 1886, 609), is, according to the latter authority, a distinct compound, having the formula $C_6H_{12}O_6$. The only crystalline derivative of formose is the osazone, which, according to Loew, has the formula $C_{18}H_{22}N_4O_3$. The author finds that this osazone is a mixture of at least two, perhaps three or four osazones. One of these, $C_{18}H_{22}N_4O_4$, is the normal osazone of a sugar, $C_6H_{12}O_6$; it was obtained in very slender, yellow needles, which began to soften at 130°, and melted completely at 144°. It is therefore impure, but the other compounds present are perhaps simply isomerides. It is comparatively readily soluble in hot water, and dissolves very readily in alcohol and ethyl acetate, far less readily in benzene.

A second osazone, which is sparingly soluble in ether and ethyl acetate, and can therefore be separated from the preceding compound by this means, gave results on analysis which agreed for the mean of the two formulæ $C_{17}H_{20}N_4O_3$ and $C_{18}H_{22}N_4O_4$.

A third osazone, which is only present in small quantities, was isolated. In melting point, which is above 204°, and its very sparing solubility in hot alcohol, it resembles phenylglucosazone and α-phenylacrosazone.

Methylenitan yields an osazone which has in general the same properties as the compound obtained from formose. Loew's statement (this vol., p. 572) that methylenitan does not yield an osazone, and is on that account quite different from formose, is therefore incorrect.

F. S. K.

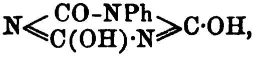
Franceïns. By C. ISTRATI (*Compt. rend.*, **106**, 277—280).—Benzene and its chloro-, nitro-, and other derivatives yield a *franceïn* when heated with strong sulphuric acid (compare this vol, p. 259), the proportion of franceïn obtained increasing with the proportion of chlorine in the benzene-derivative. All the franceïns are soluble in strong sulphuric acid, and some are soluble in water. With two exceptions, they dissolve in alkalis and form neutral salts very soluble in water. They are all more or less soluble in alcohol, forming highly coloured and strongly dichroic solutions. They dye cotton, linen, and especially silk, with shades varying from rose colour to maroon. The depth of colour and the tinctorial power of the franceïns increase with the proportion of chlorine.

The franceïns from benzene, methylbenzene, and mono- and di-chlorobenzene are black, but they become redder and acquire a conchoidal fracture and a dark-green metallic lustre, as the proportion of chlorine increases.

The action of sulphuric acid on pentachlorobenzene yields two franceïns (*loc. cit.*). The first has a deep green metallic lustre, and dissolves in potash, methyl, ethyl, and amyl alcohols and glycerol, but is insoluble in water. Its solution shows intense red-green dichroism, and dyes silk a rose colour. The second is formed in much smaller quantity, and is soluble in warm water, but is almost insoluble in potash, and is much less soluble in alcohol than the first franceïn. It dyes silk a peach colour. The first franceïn forms salts which differ in their solubility in water and alcohol, and also in their dichroism. Both franceïns have the composition $C_{18}HCl_5O_5$, and seem to have the functions of a phenol and a diquinone.

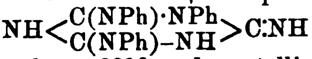
C. H. B.

Phenylisocyanuric Acid: a Fourth Triphenylmelamine. By B. RATHKE (*Ber.*, **21**, 867—873).—When the triphenylamine previously described by the author (Abstr., 1887, 662) is heated with concentrated hydrochloric acid at 160—170°, it is converted, with elimination of aniline, into *phenylisocyanuric acid*,

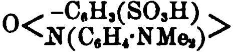


$$N\left<\begin{matrix}CO\text{-}NPh\\C(OH)\cdot N\end{matrix}\right>C\cdot OH,$$

this crystallises in flat needles, melts at 285—289° (uncorr.), and is readily soluble in hot water. The silver salt crystallises in lustrous, quadratic plates.

To the description previously given of the triphenylmelamine,  $NH\left<\begin{matrix}C(NPh)\cdot NPh\\C(NPh)\text{-}NH\end{matrix}\right>C{:}NH$ (*loc. cit.*), the following is added. It melts at 221°, and crystallises in small prisms. The hydrochloride and sulphate are very readily soluble in water, the nitrate less so; a definite platinochloride was not obtained. When heated with hydrochloric acid at 100—150°, or when heated with alcohol and a little ammonia at 150°, it is converted into normal triphenylmelamine, aniline, and diphenylmelamine, melting at 202—204°.

Fresh proof of the correctness of the formula usually assigned to normal triphenylmelamine was obtained by heating it with hydrochloric acid at 180°, when it yielded cyanuric acid, showing that the phenyl-groups were not in direct union with the ring. Hofmann's statement that normal triphenylmelamine is destitute of basic properties is incorrect. The salts are insoluble in water and very unstable; the *platinochloride*, $(C_{21}H_{18}N_6)_2,H_2PtCl_6$, crystallises in needles. When the platinochloride in alcoholic solution is treated with zinc-dust, it yields a new base crystallising in silvery, six-sided plates, and melting at 146°. A. J. G.

Dimethylanilinequinonimide. By J. FOGH (*Ber.*, 21, 887—890).—If paramidophenolsulphonic acid, made into a thin paste with water, is treated with chlorine until complete solution takes place (compare Hirsch, Abstr., 1887, 834), and the excess of chlorine is removed by the addition of small quantities of the acid until no more is dissolved, a solution of quinonechlorimidesulphonic acid is obtained, which on the addition of dimethylaniline becomes bluish-violet owing to the formation of the *dimethylaniline*-derivative of quinonimidesulphonic acid,  $O\left<\begin{matrix}\text{-}C_6H_3(SO_3H)\\N(C_6H_4\cdot NMe_2)\end{matrix}\right>$. This separates in flocks having a bronze lustre, and consisting of microscopic needles which contain ½ mol. H_2O, are practically insoluble in cold water, ether, and benzene, and sparingly soluble in hot alcohol, but are readily soluble in aqueous alkalis, yielding intensely blue solutions from which acids precipitate the compound unchanged. The compound dissolves in concentrated sulphuric acid with a cherry-red colour, is decolorised by boiling with dilute mineral acids, and when heated at 100° or treated with reducing agents, is converted into a leuco-derivative. It is probably identical with the compound obtained by Schmitt and Andresen from trichloroquinonechlorimide and dimethylaniline (Abstr., 1882, 400).

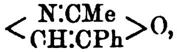
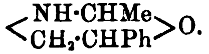
Dimethylanilinequinonimide (phenol-blue) can be prepared by adding dimethylaniline (50 grams) to a concentrated aqueous solution of oxalic acid (50 grams) containing quinonechlorimide (30 grams) in suspension, and shaking the mixture until complete solution occurs. The blue colour of the solution then changes to green, and green flocks of the oxalate separate, from which the dimethylaniline-derivative can be obtained by treatment with cold aqueous soda. It is identical with the compound obtained by Möhlau from dimethylphenylene-green (Abstr., 1886, 146).

Quinonechlorimide is best prepared by reducing 100 grams of paranitrophenol with 100 grams of tin and 500 to 600 grams of concentrated hydrochloric acid, filtering, diluting to 1 litre, and treating the solution, further diluted with four times its volume of water, and cooled to 5°, in small quantities at a time with bleaching-powder solution until both the precipitate and solution are coloured a pure yellow; the precipitate then only requires to be washed. The yield amounts to 70—80 per cent. of that theoretically possible.

W. P. W.

Base from Bromacetophenone and Acetamide. By M. Lewy (*Ber.*, **21**, 924—931; compare this vol., p. 55).—The base from bromacetophenone and acetamide yields benzoic acid when oxidised with a very dilute permanganate solution. Fuming nitric acid converts it into a *nitro*-derivative, $NO_2 \cdot C_{10}H_8NO$, which crystallises in long, bright-yellow needles, melts at 156—157°, is readily soluble in hot alcohol and benzene, insoluble in water, and on oxidation with dilute permanganate solution yields paranitrobenzoic acid. When treated with stannous chloride and hydrochloric acid, it is reduced to the *amido*-derivative, $NH_2 \cdot C_{10}H_8NO$; this crystallises in long, lustrous, colourless needles, melts at 114—115°, is readily soluble in alcohol, ether, and hot water, and readily yields a diazo-compound, which forms with dimethylaniline a violet, with resorcinol a yellow, and with β-naphthol a red colouring matter.

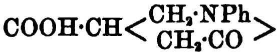
The *tetrahydro*-base, $C_{10}H_{13}NO$, is obtained by gradually adding sodium in large excess to a boiling alcoholic solution of the acetamide base. It is a colourless oil of repulsive odour, boils at 248—251°, and is readily soluble in alcohol, ether, and concentrated acids. The *benzoyl*-derivative, $C_{10}H_{12}BzNO$, crystallises in small, white, concentrically grouped needles, melts at 140°, and is readily soluble in hot alcohol, ether, and benzene.

The acetamide-base does not react with hydroxylamine, phenylhydrazine, or phosphorus pentachloride, and is not decomposed on distillation either with soda-lime or with zinc-dust. When heated with hydriodic acid and amorphous phosphorus for 12 hours at 210°, it is converted into a hydrocarbon, $C_{16}H_{16}$, which boils at 270—280°, and seems to be identical with a compound obtained by Graebe from acetophenone under similar conditions (this Journal, 1875, 457). The author regards the acetamide-base as a methylphenyloxyazole, and ascribes to it the formula  $<{N:CMe \atop CH:CPh}>O$, and to its tetrahydro-derivative the formula  $<{NH \cdot CHMe \atop CH_2 \cdot CHPh}>O$.

W. P. W.

Action of Phosphorus Pentachloride on Anilic Acids of Bibasic Acids. By R. ANSCHÜTZ (*Ber.*, **21**, 957).—Anilic acids (this vol., pp. 277 and 367) can be readily converted into the corresponding *anils* by the action of an equivalent quantity of phosphorus pentachloride on the acid suspended in chloroform.

Succinanil, succinparatolil, succinorthotolil, and succin-α-naphthil, &c., were prepared by this method. Fumaranilic acid yields a product, the formula of which agrees with that of monochlorosuccinanil. F. S. K.

Itaconanilic Acid. By R. ANSCHÜTZ and F. REUTER (*Ber.*, **21**, 958—959).—The authors have shown that the itaconanilic acid which they obtained (this vol., p. 277) is different from that prepared by Gottlieb (*Annalen*, **77**) and by Michael. In this article they discuss the formula of Gottlieb's and Michael's acid, and give  $COOH{\cdot}CH{<}\begin{matrix}CH_2{\cdot}NPh\\CH_2{\cdot}CO\end{matrix}{>}$ as the most probable. F. S. K.

Chloronitrobenzoic Acids. By A. CLAUS and H. KURZ (*J. pr. Chem.* [2], **37**, 196—201).—The substances described in this paper have been prepared from the corresponding amido-compounds by Sandmeyer's reaction.

Parachlorometanitrobenzonitrile, $NO_2{\cdot}C_6H_3Cl{\cdot}CN$, dissolves readily in alcohol, ether, chloroform, and hot water, from which it crystallises in colourless needles, melting at 100—101° (uncorr.). When boiled with dilute sulphuric acid, it forms *parachlormetanitrobenzoic acid*, which crystallises in pale-yellow needles, melting at 178—179° (uncorr.).

Parachlororthonitrobenzonitrile dissolves readily in alcohol, ether, and hot water. It forms colourless needles, melting at 98° (uncorr.). Parachlororthonitrobenzoic acid crystallises from hot water in long, colourless needles, melting at 139° (uncorr.). The sodium salt (6 mols. H_2O) is very soluble in water, from which it crystallises in flat needles. The potassium, copper, barium, ammonium, calcium, and silver salts are described.

Metachloroparanitrobenzonitrile crystallises from alcohol, ether, and hot water in colourless needles, melting at 87° (uncorr.). *Metachloroparanitrobenzoic acid* forms long, white needles, melting at 185—186° (uncorr.), and is very soluble in alcohol, ether, chloroform, and hot water. The ammonium, silver, barium (2 mols. H_2O), and calcium (2 mols. H_2O) salts are all soluble in hot water, and crystallise in colourless needles. The ammonium salt dissociates at 100°.

G. T. M.

Hydroxy-β-isodurylic Acid. By C. KROHN (*Ber.*, **21**, 884—886).—*Hydroxy-β-isodurylic acid*, $OH{\cdot}C_6HMe_3{\cdot}COOH$ [$Me_3 : OH : COOH = 1 : 3 : 4 : 6 : 5$], is obtained when the sodium-derivative of pseudocumenol is heated with excess of liquid carbonic anhydride at 170 to 180°. It crystallises in snow-white needles, melts at 181°, and at a slightly higher temperature decomposes into pseudocumenol and carbonic anhydride. It is readily soluble in ether, sparingly in the other organic solvents; the alcoholic solution gives a permanent blue coloration with ferric chloride. When treated with a mixture of acetic and nitric acids, it yields Auwers' nitropseudocumenol nitrate

(Abstr., 1885, 380). When a solution of the acid in concentrated sulphuric acid is heated at 50—70°, carbonic anhydride in abundantly evolved, and Reuter's pseudocumenolsulphonic acid (Abstr., 1878, 413) is formed. A. J. G.

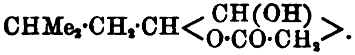
Oxidation of Unsaturated Acids. By R. Fittig (*Ber.*, **21**, 919—921).—The oxidation of the following unsaturated acids was effected by gradually adding the equivalent quantity (1 mol. to 1 mol. of the acid) of a 2 per cent. permanganate solution to a very dilute aqueous solution of the alkaline salt of the acid cooled to 0°. The yield is good, and the products can be purified with little difficulty.

The α-β-unsaturated acids yield dihydroxy-acids, which do not undergo change when boiled with dilute hydrochloric acid. Cinnamic acid, for example, is converted into phenylglyceric acid together with small quantities of benzaldehyde and oxalic acid, and ethylcrotonic acid is oxidised to the dihydroxy-acid,

$$OH{\cdot}CHMe{\cdot}CEt(OH){\cdot}COOH,$$

which crystallises well, melts at 95—96°, and is not identical with How's hexeric acid obtained in very small quantity in the decomposition of the dibromide of ethylcrotonic acid.

The β-γ-acids yield dihydroxy-acids which, when warmed with dilute hydrochloric acid, readily undergo conversion into the corresponding hydroxy-lactones. Thus, isophenylcrotonic acid forms the beautifully crystalline *phenylhydroxybutyrolactone*, $OH{\cdot}CH{<}\begin{matrix}CH_2{\cdot}CO\\CHPh\end{matrix}{>}O, + \frac{1}{2}H_2O$, which melts at 76—77°, or, when anhydrous, at 86—87°. The corresponding *phenyldihydroxybutyric acid*, $OH{\cdot}CHPh{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, forms large crystals, and melts at 116°, with decomposition into the hydroxy-lactone. Isoctylenic acid, $CHMe_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$, obtained by the distillation of isobutylparaconic acid, is in like manner converted into the liquid hydroxy-lactone,



$$CHMe_2{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CH(OH)\\O{\cdot}CO{\cdot}CH_2\end{matrix}{>}.$$

The γ-δ-acids, as, for example, cinnamenylpropionic acid and hydrosorbic acid, also yield hydroxy-lactones, which differ, however, in many respects from those obtained from the β-γ-acids. The research, which has been carried on in conjunction with the author's pupils, is being continued. W. P. W.

Iodophenolsulphonic Acids. By F. Kehrmann (*J. pr. Chem.* [2], **37**, 9—14).—When iodine (1 mol.), in the form of a mixture of potassium iodide and iodate, is added little by little to potassium paraphenolsulphonate (1 mol.) dissolved in excess of dilute hydrochloric or sulphuric acid, iodine at first separates, but is quickly reabsorbed, and after a short time the liquid crystallises to a dense mass of long, thin prisms of the formula $C_6H_3I_2O{\cdot}SO_3K + 2H_2O$. This salt begins to decompose at 270° without melting. The barium salt, $(C_6H_3I_2O{\cdot}SO_3)_2Ba + 3H_2O$, is only slightly soluble in cold water from which it crystallises in white, glistening needles. The copper salt forms pale green, monoclinic prisms. The anhydrous free acid melts at 120°, and decomposes with separation of iodine at 190°. It dissolves readily in water from which it is precipitated by hydrochloric or sulphuric acid. It probably has the constitution [$HO : I_2 : SO_3H = 1 : 2 : 6 : 4$].

The mother-liquor on evaporation yields a considerable quantity of unchanged potassium paraphenolsulphonate, and an amount insufficient for analysis of a substance containing iodine, and crystallising in gleaming scales. G. T. M.

Iodophenolsulphonic Acids. By E. OSTERMAYER (*J. pr. Chem.* [2], **37**, 213—216).—If paraphenolsulphonic acid (1 mol.) is treated with iodine (1 mol.) in the way described by Kehrmann (this vol., p. 595), besides the chief product, diiodophenolsulphonic acid, a compound is produced which appears to be a moniodosulphonic acid. This acid forms thick, colourless crystals belonging to the rhombic system, and differs from the diiodosulphonic acid by its barium and calcium salts dissolving readily in water. The diiodosulphonic acid forms a zinc salt, $(OH\cdot C_6H_2I_2\cdot SO_3)_2Zn + 6OH_2$, which crystallises in long, colourless needles. The paper is mainly on the question of priority between the author and Kehrmann (*loc. cit.*). G. T. M.

New Synthesis of Tetraphenylethylene. By J. H. ZIEGLER (*Ber.*, **21**, 779—781).—When equivalent quantities of sulphur and diphenylmethane are heated together, the former begins to dissolve at 110°, and the solution is complete at 150°; the scarcely yellow solution yields crystals of unaltered sulphur on cooling. On raising the temperature, the liquid slowly darkens at 200°, and an evolution of hydrogen sulphide begins; the reaction requires 10 hours' heating at 240—290° for completion. The residue consists mainly of tetraphenylethylene, and can be purified by treatment with ether in which unaltered diphenylmethane, &c., dissolve. The yield is about 75 per cent. of the diphenylmethane employed. A. J. G.

Action of Chlorine on α- and β-Naphthol. By P. T. CLEVE (*Ber.*, **21**, 891—896).—*Dichloro-α-naphthol*, $C_{10}H_5Cl_2\cdot OH$ (probably $OH : Cl : Cl = 1 : 2 : 4$), is obtained, together with chloro-α-naphthol, by the action of chlorine on a cold solution of α-naphthol in acetic acid. It crystallises from alcohol, chloroform, and benzene in silky needles melting at 106°, and from acetic acid in prisms having the composition $C_{10}H_5Cl_2\cdot OH + C_2H_4O_2$; these lose the associated acetic acid completely at 40—50°. When heated at 170—180°, it loses hydrogen chloride, and is converted into a compound which probably has the composition $C_{20}H_{10}Cl_2O_2$, does not melt at 275°, and is insoluble in all the ordinary solvents. On oxidation with dilute nitric acid, dichloro-α-naphthol yields phthalic acid and a quinone-like compound crystallising in yellow needles, whilst *chloronaphthaquinone*, $C_{10}H_5ClO_2$, is formed when it is treated with chromic acid in acetic acid solution; this crystallises in lustrous, golden-yellow needles, melts at 116°, is soluble in alcohol, and yields an *anilide*, $C_{10}H_4ClO_2\cdot NHPh$, which forms sparingly soluble, purple-red crystals and melts at 202—203° (compare Knapp and Schultz, Abstr., 1882, 510; Claus, *Ber.*, **18**, 2929). When treated with phosphorus pentachloride, dichloro-α-naphthol is converted into a *trichloronaphthalene* (= 1 : 2 : 4?), which crystallises in needles and melts at 92°.

Chloro-α-naphthol (probably OH : Cl = 1 : 2), owing to its great solubility in the ordinary solvents, could only be crystallised from light petroleum. It could not, however, be obtained pure either by distillation or by fractional crystallisation; the impure crystals melted at about 54°. When treated in acetic acid solution with chlorine, it is converted into the dichloro-derivative, whilst phosphorus pentachloride reacts with it to form the above trichloronaphthalene.

Chloro-β-naphthol, $C_{10}H_6Cl\cdot OH$, is obtained under like conditions from β-naphthol. It crystallises from chloroform in monoclinic forms, $a : b : c = 1\cdot9600 : 1 : 1\cdot9562$; $\beta = 66° 54'$; observed faces, $0P$, $\infty\bar{P}\infty$, $+\bar{P}\infty$, $-\bar{P}\infty$, ∞P, melts at 70°, and is readily soluble in alcohol, benzene, chloroform, acetic acid, and boiling light petroleum; it is also soluble in hot water from which it crystallises in talc-like scales. When heated with phosphorus pentachloride, it yields a dichloronaphthalene melting at 34° (compare Abstr., 1887, 961), and also the *orthophosphate*, $(C_{10}H_6ClO)_3PO$, which crystallises from alcohol in microscopic needles, melts at 152°, is insoluble in water and only very sparingly soluble in hot alcohol. W. P. W.

Investigation of the Second Van't Hoff Hypothesis. By K. Auwers and V. Meyer (*Ber.*, **21**, 784—817).—The second hypothesis which Van't Hoff deduced from his arrangement of atoms in space is that two carbon-atoms united by a single affinity are free to rotate, the axis of rotation being the bond of union, and that isomerism is only possible for those substances of the type $\equiv C—C\equiv$ which cannot by rotation round the common axis be converted into the same form. As the existence of the two isomeric dioximes of benzil, discovered by V. Meyer and H. Goldschmidt, would, if for both the formula $Ph\cdot C(NOH)\cdot C(NOH)\cdot Ph$ were established, be in direct contradiction to the above hypothesis, the present paper contains a series of investigations by which the authors have sought to ascertain whether the composition of the above two compounds is identical.

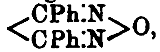
The preparation of the dioximes is that formerly described. By treating benzil in alcoholic solution with hydroxylamine hydrochloride, the α-dioxime is formed, and from this the β-dioxime may be easily obtained by simply heating with three times its weight of absolute alcohol at 170—190° for some hours. The α-dioxime separates from alcohol as a white, crystalline powder, melting with decomposition at 237°, insoluble in water, and nearly insoluble in acetic acid, ether, and alcohol, of which the last dissolves 0·05 part per 100 at 17°. The β-dioxime crystallises from alcohol in slender needles melting with decomposition at 206—207°, slightly soluble in water, and easily soluble in acetic acid, ether, and alcohol, of which the last dissolves 15·26 parts per 100 at 17°. Of the two forms, the latter is the more stable into which the first is readily converted, but change in the opposite direction never takes place. Thus the α- is converted into the β-dioxime when it is heated with alcohol at 170°, or with water at

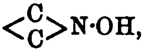
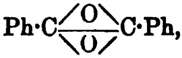
200°, also when it is treated with acetic chloride or with hydrogen chloride in acetic acid solution. Both are true derivatives of benzil, as both yield benzil and hydroxylamine hydrochloride when heated with concentrated hydrogen chloride in a sealed tube at 100°. The change takes place somewhat less readily with the β- than with the α-compound.

The non-existence of true nitroso-groupings in either compound is shown by each yielding a diacetyl-derivative when treated with acetic anhydride. *α-Diacetyldiphenylglyoxime* melts at 147—148°, is insoluble in water, and sparingly soluble in alcohol and acetic acid. *β-Diacetyldiphenylglyoxime* melts at 124—125°, and is easily soluble in alcohol and acetic acid, from the hot solutions of which it crystallises in fine needles. On treatment with alkalis, both derivatives yield the oximes from which they were prepared.

To further remove all doubt as to the possibility of merely physical isomerism, and to prove that the oximes are not only different from one another, but yield different derivatives, reconvertible into their respective oximes, the propionic and isobutyric derivatives were also prepared.

Dipropionyldiphenylglyoxime.—The α-derivative is easily soluble in alcohol, acetic acid and ether, and crystallises in thin scales melting at 103—104°; the β-derivative is slightly soluble in alcohol and acetic acid, soluble in ether, crystallises in oblique prisms, and melts at 121°. *Diisobutyryldiphenylglyoxime.*—The α-derivative is easily soluble in alcohol, ether, and acetic acid, and crystallises in flat needles melting at 121—122°; the β-derivative is very soluble in alcohol, ether, and acetic acid, crystallises in quadratic prisms melting at 88—89°, below which temperature the substance begins to sublime.

The two oximes were oxidised by means of potassium ferricyanide, and both were found to give the same oxidation-product—that described by Koreff (Abstr., 1886, 363). By reduction of this product with hydriodic acid, pure dibenzyl is obtained, thus proving the presence of the Ph·C·C·Ph-group in the original compounds and the oxidation-product, and confirming Koreff's view of the constitution of the latter. Hence it is a polymeride and not, as Gabriel (Abstr., 1886, 693) assumed, an isomeride of phenyl cyanate, which it furnishes on strongly heating. An attempt by reduction to again obtain either of the oximes failed, but a *dioxime-anhydride*,  $<^{\mathrm{CPh:N}}_{\mathrm{CPh:N}}>\mathrm{O}$, melting at 94° was obtained.

In order to ascertain whether there was any tendency towards the formation of the group  $<^{\mathrm{C}}_{\mathrm{C}}>\mathrm{N{\cdot}OH}$, attempts were made to prepare compounds containing this group from stilbene bromide by treatment with hydroxylamine and nitrous acid. These, however, failed to yield any product of an oxime character, as also did the treatment with amyl nitrite and sodium alcoholate. Isobenzil,  $\mathrm{Ph{\cdot}C}{<^{\mathrm{O}}_{\mathrm{O}}>}\mathrm{C{\cdot}Ph}$, when heated with hydroxylamine hydrochloride and absolute alcohol at 140—150°, did appear to yield the β-dioxime, but under the conditions of the experiment it must be assumed that the isobenzil is converted into benzil, and that the latter yields the dioxime.

Both oximes, when heated in sealed tubes with water for some hours at a temperature above 200°, yield one and the same anhydride, the dioxime-anhydride melting at 94° before mentioned. It crystallises in flat needles, moderately soluble in cold alcohol, easily soluble in ether and acetic acid. As the formation of the anhydride takes place at a temperature above that at which the α- is converted into the β-dioxime, a direct formation from the α-derivative does not occur and has not yet been found possible. The anhydride is also obtained on heating the diacetyl-derivative with alcohol at 170—190°. It is a stable substance, can be heated with alkalis for hours, or with hydrogen chloride in a sealed tube, or even with hydrogen iodide for some time without change. Only on heating for at least 10 hours with hydrogen iodide at 230° does it yield dibenzyl. The formation of only one and the same anhydride from the isomeric dioximes is similar to the formation of the same anhydride from fumaric and maleic acids.

In order to prove that the compound obtained by Beckmann (Abstr., 1887, 827), by heating the dioxime with sulphuric acid, was no anhydride, it was prepared and examined by treatment with hydrogen iodide. It gave not dibenzyl but benzoic acid, showing that intramolecular change had undoubtedly taken place. The above compound could only be obtained from the α-dioxime.

The determination of the molecular weights by Raoult's method, which has been already described (this vol., pp. 407, 408) gave practically the same value for each dioxime. The α-compound gave 333, the β-compound 320—the theoretical value being 324.

By these results, then, the identity of the two dioximes in chemical composition has been established, and it is therefore thought necessary that the second Van't Hoff hypothesis must in so far be altered as to admit of some cases in which free rotation round the axis cannot take place, as otherwise no explanation of the isomerism is possible.

H. C.

β-Tetrahydronaphthylamine. By E. BAMBERGER and R. MÜLLER (*Ber.*, **21**, 847—860).—β-Tetrahydronaphthylamine (this vol., p. 159) is best prepared by allowing a boiling solution of β-naphthylamine (15 grams) in absolute amyl alcohol (170—180 grams) to flow in a continual stream on to sodium (12 grams) contained in a flask connected with a good condenser; the mixture is then heated so that the temperature does not fall below the boiling point of the amyl alcohol until the whole of the sodium has dissolved. The product is poured into water and the upper layer separated. The bases are converted into hydrochlorides, dissolved in hot water, mixed with excess of soda, and the separated bases dissolved in ether. The ethereal solution is well cooled, and a stream of steam saturated with carbonic anhydride is passed into the liquid, when β-tetrahydronaphthylamine carbonate is completely precipitated in a nearly pure condition, whilst the unaltered β-naphthylamine remains in solution. Dihydronaphthalene is formed as a bye-product in the reaction. Tetrahydronaphthylamine is a colourless, slightly viscid liquid, turning brown if exposed to the air for some time, and has an intense ammoniacal, piperidine-like odour; it boils at 162° under 36 mm. pressure, and at 249·5° under 710 mm. (corr.), in the last case with slight decomposition;

sp. gr. 1·031 at 16°. It is but little soluble in water, readily soluble in the organic solvents. It is one of the strongest organic bases, eagerly absorbs carbonic anhydride from the air, has a strongly alkaline reaction, and does not yield colouring matters with diazo-compounds; in all these respects differing markedly from β-naphthylamine. When oxidised, it yields a carboxyphenylpropionic acid (1 : 2), whilst β-naphthylamine gives phthalic acid.

The salts of β-tetrahydronaphthylamine are all more or less soluble in water, and crystallise well. The *carbonate*, $(C_{10}H_{11}\cdot NH_2)_2,H_2CO_3$, forms lustrous, white needles; the *hydrogen carbonate*,

$$C_{10}H_{11}\cdot NH_3\cdot HCO_3,$$

is a white, granulo-crystalline powder; the *hydrochloride*,

$$C_{10}H_{11}\cdot NH_2,HCl,$$

forms silvery-white tables, and melts at 237°; the *sulphate* forms lustrous, white prisms; the *dichromate* crystallises in orange-yellow prisms; the *platinochloride*, $(C_{10}H_{11}\cdot NH_2)_2,H_2PtCl_6$, forms satiny, orange-yellow prisms; the *aurochloride* forms golden-yellow needles; the *mercurochloride* is very characteristic—it is precipitated in silky, interlaced needles converted on recrystallisation from boiling water into inch-long prisms of vitreous lustre melting at 241·5°. The *hydrobromide*, *picrate*, and *ferrocyanide* are also described. The *acetyl*-derivative, $C_{10}H_{11}\cdot NHAc$, melts at 107·5°, the *benzoyl*-derivative at 150—151°.

The *nitrite*, $C_{10}H_{11}\cdot NH_2,HNO_3$, is prepared by passing nitrous gases into a well-cooled solution of the base in dry ether; it crystallises in tufts of long, silky needles or in short, strongly-refractive prisms, and melts at 160° with decomposition. It is characterised by the most extraordinary stability; its aqueous solution can be boiled for days without the least trace of decomposition: from this cause the authors were not able to prepare β-tetrahydronaphthol.

β-Tetrahydronaphthylamine tetrahydronaphthylthiocarbamate (*loc. cit.*) forms long, lustrous needles and melts at 142°. *Di-β-tetrahydronaphthylthiocarbamide*, $CS(NH\cdot C_{10}H_{11})_2$, prepared by boiling the preceding compound with alcohol, crystallises in stellate groups of lustrous, white needles, and melts at 161° with decomposition.

β-Tetrahydronaphthylphenylcarbamide, $NHPh\cdot CO\cdot NH\cdot C_{10}H_{11}$, prepared by the action of phenyl cyanate on the tetrahydro-base, crystallises in concentrically-grouped, long, silky needles, and melts at 166·5°.

A. J. G.

Bases from Dinaphthylthiocarbamide. By F. Evers (*Ber.*, **21**, 962—977).—Numerous experimenters have shown that ethereal salts, the constitution of which is $NH:C(NH_2)\cdot SR$, are formed by the action of haloid alkyl-derivatives on thiocarbamides.

Methyl α-naphthylimidonaphthylthiocarbamate,

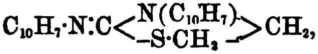
$$C_{10}H_7\cdot N:C(SMe)\cdot NH\cdot C_{10}H_7,$$

is obtained by acting on α-naphthylthiocarbamide with methyl iodide and treating the product with soda; it crystallises in colourless, flat prisms melting at 136°, is almost insoluble in cold alcohol, dissolves slowly in hot alcohol and ether, and is very stable. The *hydriodide*, $C_{22}H_{18}N_2S,HI$, forms small, colourless crystals which melt at 174° and become yellow and insoluble on exposure to the light. The *platinochloride*, $(C_{22}H_{18}N_2S)_2,H_2PtCl_6$, is a yellow, crystalline powder, sparingly soluble in hot water and hot alcohol; it melts at 202° with decomposition. On heating the base, it yields α-carbodinaphthylimide and mercaptan, and when heated with alcoholic potash, α-dinaphthylcarbamide is obtained.

Ethyl α-naphthylimidonaphthylthiocarbamate, obtained in a similar manner to the methyl salt, forms large, prismatic crystals which melt at 98°, and are only sparingly soluble in hot alcohol. The *hydriodide* crystallises in clusters of colourless needles melting at 157°; it is very sparingly soluble in hot water, and turns yellow on exposure to the light. The *platinochloride*, $(C_{23}H_{20}N_2S)_2,H_2PtCl_6$, forms small, yellow needles. The behaviour of this base towards alkalis, and on heating, is similar to that of the methyl-derivative.

Propyl α-naphthylimidonaphthylthiocarbamate crystallises in large, nacreous leaves melting at 95°. The *hydriodide* forms fine, shining needles which melt at 97°, and are very sparingly soluble in water even on addition of hydrochloric acid.

Ethylene α-naphthylimidonaphthylthiocarbamate,



$$C_{10}H_7{\cdot}N{:}C{<}\begin{matrix}N(C_{10}H_7)\\-S{\cdot}CH_2-\end{matrix}{>}CH_2,$$

crystallises in groups of concentric, colourless needles melting at 139°; it dissolves slowly, but to a considerable extent in alcohol. The *platinochloride*, $(C_{23}H_{18}N_2S)_2,H_2PtCl_6$, is a yellow, crystalline powder which dissolves in a large quantity of hot water or alcohol, and decomposes when heated above 200°.

Methyl β-naphthylimidonaphthylthiocarbamate, crystallises in clusters of small needles melting at 110°; it is very readily soluble in warm alcohol and ether. This compound is very unstable. The *platinochloride* crystallises in stellate forms which decompose above 150° without melting.

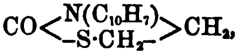
Ethyl β-naphthylimidonaphthylthiocarbamate forms shining, silky needles melting at 106°, and is less stable than the methyl-derivative. The *platinochloride* forms small, yellow crystals which decompose above 155° without melting.

Propyl β-naphthylimidonaphthylthiocarbamate crystallises in very small concentric needles which melt at 65—66°, and are readily decomposed. The *platinochloride* is a yellow, crystalline compound which decomposes above 120° without melting.

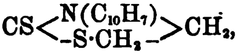
Ethylene β-naphthylimidonaphthylthiocarbamate crystallises from hot alcohol in silvery leaves melting at 172°. This base is tolerably stable, but turns reddish on exposure to the light. The *platinochloride*, $(C_{23}H_{18}N_2S)_2,H_2PtCl_6$, is a yellow, crystalline powder which decomposes above 146° without melting.

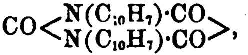
When the α-methyl base, described above, is heated with absolute alcoholic ammonia, α-dinaphthylguanidine is produced. *α-Trinaphthylguanidine*, $C_{10}H_7{\cdot}N{:}C(NH{\cdot}C_{10}H_7)_2$, is produced by heating the α-methyl base with α-naphthylamine in alcoholic solution; it forms colourless, flat, needle-shaped crystals, melts at 178°, is insoluble in water, and only sparingly soluble in dilute acids, but dissolves in considerable quantities in hot alcohol, although slowly.

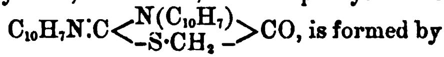
Methyl α-naphthylthiocarbamate, $C_{10}H_7\cdot NH\cdot COSMe$, is formed by heating the α-methyl base with dilute sulphuric acid; it crystallises in groups of small, colourless needles melting at 122°, and dissolves readily in dilute alcohol, ether, and benzene, but is insoluble in water, dilute acids, and dilute alkalis. When heated with alcoholic ammonia, it yields α-mononaphthylcarbamide.

Ethylene α-naphthylthiocarbamate,  $CO<\begin{matrix}N(C_{10}H_7)\\-S\cdot CH_2-\end{matrix}>CH_2$, is obtained when the α-ethylene base is heated with dilute hydrochloric acid; it crystallises in groups of small, almost colourless needles melting at 102°.

Methyl α-naphthyldithiocarbamate, $C_{10}H_7\cdot NH\cdot CSSMe$, is produced when the α-methyl base is heated with carbon bisulphide; it crystallises in small needles which melt at 185°, and dissolves tolerably readily in hot alcohol or ether, but is insoluble in water and dilute acids.

Ethylene α-naphthyldithiocarbamate,  $CS<\begin{matrix}N(C_{10}H_7)\\-S\cdot CH_2-\end{matrix}>CH_2$, crystallises from alcohol in narceous leaves melting at 198—199°; it is insoluble in dilute acids and alkalis.

α-Dinaphthylparabanic acid,  $CO<\begin{matrix}N(C_{10}H_7)\cdot CO\\N(C_{10}H_7)\cdot CO\end{matrix}>$, is obtained by treating the methyl base with cyanogen-gas in alcoholic solution; it crystallises in needles which melt at 246° and dissolve slowly, but to a considerable extent, in hot alcohol; it is sparingly soluble in ether, but insoluble in water and dilute acids. When treated with alcoholic potash, it yields carbonic anhydride, oxalic acid, and α-naphthylamine.

α-Dinaphthylthiohydantoïn,  $C_{10}H_7N:C<\begin{matrix}N(C_{10}H_7)\\-S\cdot CH_2-\end{matrix}>CO$, is formed by the action of monochloracetic acid on α-dinaphthylthiocarbamide; it crystallises in shining, yellow leaves, melts at 176°, is insoluble in water, but dissolves to a considerable extent, although slowly, in hot alcohol.

β-Dinaphthylthiohydantoïn resembles the preceding compound, and melts at 174°.

Ethyl, propyl, and allyl phenyldithiocarbamates all yield phenyldithiocarbamide glycolide when treated with monochloracetic acid; similarly the ethereal salts of ortho- and para-tolyldithiocarbamic acid yield the corresponding tolyldithiocarbimide glycolide. Ethylene phenyldithiocarbamate yields thioglycollic acid and ethylene phenylthiocarbamate by a similar treatment, and the ethylene ethereal salts of α-naphthyl-, ortho- and para-tolyldithiocarbamic acid behave in the same way. F. S. K.

Dichlor-α-naphthaquinonesulphonic Acid. By A. Claus and Schoneveld van der Cloet (*J. pr. Chem.* [2], **37**, 181—196).—The *sodium dichlor-α-naphthaquinonesulphonate* is prepared by treating 100 grams of sodium dinitro-α-naphtholsulphonate with 3 litres of hydrochloric acid (sp. gr. 1·09) and mixing the resulting pulp with

100 grams of sodium chlorate. After one day, the yellow solution is evaporated, and then deposits a bright-yellow, crystalline powder of the composition $C_{10}H_3O_2Cl_2{\cdot}SO_3Na$. The acid is obtained by carefully decomposing the barium salt with sulphuric acid. It dissolves readily in water and alcohol, and crystallises from hot hydrochloric acid in glistening yellow plates melting at 229° (uncorr.). The sodium salt is only slightly soluble in water, and crystallises from alcohol in yellow scales. With acid potassium sulphate, it forms a double salt of an intense yellow colour. The barium, calcium, lead, and silver salts are all anhydrous, and but slightly soluble in water.

When a solution of dichlor-α-naphthaquinonesulphonic acid is boiled with zinc and hydrochloric acid, the solution first becomes violet and eventually colourless. The violet solution gives with barium chloride a pale-red precipitate containing 18·19 per cent. of barium. It is probably the unstable quinol compound.

Dichlor-α-naphthaquinonesulphonic acid, like dichlor-α-naphthaquinone, when boiled with potash or soda, readily exchanges one of its atoms of chlorine for hydroxyl. *Hydroxychlor-α-naphthaquinonesulphonic acid*, $OH{\cdot}C_{10}H_3O_2Cl{\cdot}SO_3H$, is very soluble in water, slightly soluble in alcohol, but insoluble in ether and chloroform. After recrystallisation from hot hydrochloric acid, it melts at 211° (uncorr.) with decomposition. Its aqueous solution gives a dark red coloration with ferric chloride. Those salts in which only the hydrogen of the sulphonic acid-group is displaced by a metal are yellowish-red, whilst those in which the hydrogen of the hydroxyl is also displaced, are dark red. The sodium salt, $(ONa{\cdot}C_{10}H_3O_2Cl{\cdot}SO_3Na + 2H_2O$, is readily dissolved by water, but is only slightly soluble in alcohol. The barium salt, $C_{10}H_3O_6ClSBa + 2H_2O$, crystallises from hot water in microscopic needles. The silver salt, $C_{10}H_3O_2Cl(OAg){\cdot}SO_3Ag + H_2O$, is a heavy crystalline powder decomposed by heating to 170°.

By treating dichlor-α-naphthaquinone sodium sulphonate with potash and a large excess of phenol, *sodium phenoxychlor-α-naphthaquinonesulphonate*, $OPh{\cdot}C_{10}H_3O_2Cl{\cdot}SO_3Na + PhOH$, is obtained in the form of dark-yellow needles. The free acid melts with decomposition at 121° (uncorr.). The barium salt, $(OPh{\cdot}C_{10}H_3O_2Cl{\cdot}SO_3)_2Ba + 2PhOH$, crystallises from hot water in dark yellow, microscopic needles. Silver and lead salts are described.

Sodium acetoxychlor-α-naphthaquinonesulphonate,

$$OAc{\cdot}C_{10}H_3O_2Cl{\cdot}SO_3Na,$$

is obtained by heating 1 part of the disodium salt of the hydroxy-acid with 3 parts of acetic chloride in a sealed tube for eight hours at 100°. It crystallises in bright yellow needles. Both the acid and its salts are characterised by forming double salts, such as $C_{12}H_6SO_7Ag + 2AgNO_3$, and $(C_{12}H_6SO_7)_2Pb + 2Pb(OAc)_2$, both of which crystallise in red needles.

Sodium anilidochlor-α-naphthaquinonesulphonate,

$$NHPh{\cdot}C_{10}H_3O_2Cl{\cdot}SO_3Na,$$

is formed when sodium dichloronaphthaquinonesulphonate (1 mol.) is heated with aniline (2 mols.). The free acid is insoluble in ether, but readily dissolves in alcohol, and melts at 190° (uncorr.). Both the acid and its salts dye wool and silk a beautiful red, without mordants, and the colour is not changed by acids. The sodium and lead salts are described. With the toluidines and xylidines, the acid forms compounds possessed of dyeing properties.

Dichlor-α-naphthaquinonesulphonic acid has the constitution $[O_2 : Cl_2 : SO_3H = 1 : 4 : 2 : 3 : 3']$. The β-hydroxyphthalic acid obtained from it melts at 205° (uncorr.), the corresponding anhydride at 167° (uncorr.). G. T. M.

Characteristics of Partially Hydrogenised Aromatic Substances. By E. Bamberger and W. Lodter (*Ber.*, **21**, 836—846).—The bromination of a large number of these compounds has been studied. The same method was employed in all cases; the substance was dissolved in chloroform, cooled to 0°, and a solution of the calculated quantity of bromine in chloroform added drop by drop; after remaining some time in the freezing mixture, the chloroform and excess of bromine were evaporated, and the products purified by recrystallisation, &c.

Dihydronaphthalene dibromide has been already described (Abstr., 1887, 719).

Dihydroacenaphthene dibromide, $C_{12}H_{12}Br_2$, is prepared from tetrahydroacenaphthene (this vol., p. 292) as described above, its formation being accompanied by the elimination of hydrogen as hydrogen bromide. It crystallises in lustrous, thick tables, or in short, highly refractive prisms of the rhombic system; $a : b : c = 0{\cdot}9996 : 1 : 1{\cdot}0837$; observed forms, $0P$, $\bar{P}\infty$, $\breve{P}\infty$, ∞P; melts at 138°; and is sparingly soluble in cold, readily in hot alcohol, and in benzene, ether, and chloroform. When heated with alcoholic potash, it yields acenaphthene.

Bromacenaphthene, $C_{12}H_9Br$, is formed simultaneously with the compound last described, which is readily separated from it by crystallisation. It is a pale-yellow, viscid liquid, and boils at 302—307°.

Tetrahydrodiphenyl dibromide, $C_{12}H_{14}Br_2$, is a yellow liquid which cannot be distilled without decomposition, and is sparingly soluble in alcohol, readily in ether and chloroform.

Dihydrodiphenyl, $C_{12}H_{12}$, prepared by treating the preceding compound with alcoholic potash, is an oil, and boils at 247—249°. The *dibromide* is an oil which when heated, either alone or with alcoholic potash, readily loses hydrogen bromide, and is converted into diphenyl.

Bromotetrahydrodiphenyl dibromide, $C_{12}H_{13}Br_3$, is formed by the action of bromine on tetrahydrodiphenyl; it crystallises in strongly refractive, rhombic tables; $a : b : c = 0{\cdot}6998 : 1 : 0{\cdot}5376$, observed faces, $\infty\breve{P}\infty$, $\infty\breve{P}4$, $\bar{P}\infty$, $\infty\bar{P}\infty$, $\infty\breve{P}6$, P; it melts at 134°, and is sparingly soluble in alcohol and ether, more readily in chloroform and hot benzene.

Bromodihydrodiphenyl, $C_{12}H_{13}Br$, obtained by the action of alcoholic potash on the preceding compound, is a yellow oil which decomposes into diphenyl and hydrogen bromide when heated. The *dibromide* is a colourless oil which yields a mixture of diphenyl and bromodiphenyl when heated with alcoholic potash.

The authors suggest the following test for partially hydrogenised aromatic compounds. The substance is dissolved in chloroform, and a very dilute solution of bromine in chloroform added, the whole being well cooled; if the colour of the halogen disappears, the solution is evaporated to dryness after treatment with sulphurous acid to remove adhering bromine, dissolved in absolute alcohol, and heated with alcoholic potash, when the separation of potassium bromide renders it probable that the substance belongs to this class. The proof is, however, by no means certain, inasmuch as some other substances give the reaction, whilst anthracene dihydride does not give the test (probably because the additional hydrogen-atoms are attached to the carbon-atoms serving to connect the two benzene-rings). This test was applied to the following substances, the quantities of which were too small for quantitative investigation: tetrahydrophenanthrene, tetrahydroretene, dimethylpiperideïne, isonicotine, and cantharic acid, in all cases with positive results. A. J. G.

Retene from Rosin Oil. By W. Kelbe (*Chem. Centr.*, 1887, 1504, from *Ntf.-Vers. zu Wiesbaden*, **60**, 242).—Retene can be obtained by heating rosin oil with sulphur until hydrogen sulphide ceases to come off, and then distilling the product. J. P. L.

Atmospheric Oxidation of Turpentine, Camphor Oil, and Oil of Sunflower. By C. T. Kingzett (*J. Soc. Chem. Ind.*, 7, 67—69).—The author expresses the opinion that the results which led Yoshida (Trans., 1885, 779) to assert that camphorogenol isolated from camphor oil by fractional distillation constitutes the source from which camphor itself is produced, are not conclusive evidence, since, as all the operations were conducted with free access of air (which was observed by Yoshida to favour the change), it is possible that camphor was produced by the direct oxidation of the terpenes. The author has repeatedly subjected samples of camphor oil to oxidation by air in the presence of water, with the view of ascertaining if the products are identical with those which are furnished by terpenes generally, and found that hydrogen peroxide was freely produced. The formation of the latter necessitates the previous production of camphoric acid, which, unless it be identical in composition with camphorogenol, would complicate the chemistry of the oxidation of camphor oil much beyond Yoshida's expressed views. It would therefore be interesting to know whether camphorogenol yields hydrogen peroxide when brought into contact with water.

The author in experimenting with a specimen of sunflower oil failed to obtain hydrogen peroxide therefrom when oxidised by his process, and concludes that it did not contain any terpene. He was not, however, certain whether this sample was produced from the seeds of the sunflower or from the leaves. D. B.

Oil of Spike. By R. Voiry and G. Bouchardat (*Compt. rend.*, **106**, 551—553).—The crude product from Ardeche was amber coloured and had a strong odour; sp. gr. = 0·92, rotatory power, $[\alpha]_D = +1° 24'$. It was fractionated under ordinary pressure below 190°, and under reduced pressure at higher temperatures.

A small fraction boiling at 155—160° consisted of a terebenthene with a rotatory power $[\alpha]_D +24° 48'$. It gave a solid hydrochloride melting at 129° with a rotatory power $[\alpha]_D = -1° 54'$. The fraction boiling at 160—176° was likewise very small.

The fraction at 176—180°, *spikol*, amounted to one-tenth of the weight of the original substance. It has the composition $C_{10}H_{18}O$, solidifies at −25°, and melts at −3°, but after purification by cooling and partial melting, it melts at 0°, and is optically inactive, whilst the mother-liquor has a rotatory power $[\alpha]_D = +7° 0'$. The original fraction at 176—178° had a rotatory power $[\alpha]_D = +2° 16'$, and the fraction at 178—180° a rotatory power +1° 20′; sp. gr. = 0·935; vapour-density 5·4.

The purified product seems to be identical with eucalyptol or cajeputol. With hydrogen chloride, it yields a solid hydrochloride, $(C_{10}H_{18}O)_2,HCl$, which becomes liquid in contact with moist air, or with water, and when treated with water or alkalis yields the original spikol. In a vacuum it loses hydrogen chloride on slight rise of temperature. If heated with water in sealed tubes, it yields a dihydrochloride, $C_{10}H_{16},2HCl$, together with spikol. With bromine, spikol yields a cinnabar-red compound, $C_{10}H_{18}OBr_2$, insoluble in light petroleum, and identical with the compound obtained in the same way from cyneol. C. H. B.

Apiole. By G. Ciamician and P. Silber (*Ber.*, **21**, 913—914).—The authors find that apiole boils at 179° at 34 mm., and at 294° at the ordinary pressure, and that its composition is $C_{12}H_{14}O_4$ (compare v. Gerichten, this Journal, 1876, ii, 533). It is volatile with steam, and dissolves in the ordinary organic solvents, but combines neither with acids nor with bases, and does not react with hydroxylamine and phenylhydrazine. When oxidised, either in aqueous or acetic acid solution, with chromic acid mixture, it is converted into a compound, $C_{10}H_{10}O_6$, which crystallises from dilute alcohol in needles, melts at 102°, and is sparingly soluble in water and light petroleum, readily soluble in alcohol, ether, benzene, carbon bisulphide, and acetic acid. Concentrated sulphuric acid dissolves it with an intense yellow colour, which changes to olive-green on warming. A small quantity of a volatile acid is also formed during the oxidation, but the quantity obtained was insufficient to admit of its nature being determined. When apiole is oxidised with potassium permanganate, an acid and a neutral compound melting at 122° are formed. Further results are promised. W. P. W.

Strophanthin. By T. R. Fraser (*Proc. Roy. Soc. Edin.*, **124**, 370—374).—In former communications, the author described a compound to which the name strophanthin has been given, and which is obtained from the seeds of *Strophanthus hispidus*. Various seeds which have been examined since those communications do not all yield identical substances, therefore a fresh examination has been undertaken. The former and impure products obtained by means of alcohol and ether were dissolved in water, tannin was added, and the tannate precipitated with freshly precipitated lead oxide, and extracted with rectified spirit. This extract was then mixed with ether, and the precipitate finally dissolved in dilute alcohol, and the lead precipitated by carbonic anhydride. Filtration and drying in a vacuum yielded a translucent, gummy mass, which afterwards became white and opaque. This strophanthin is faintly acid, of an intense, bitter taste, freely soluble in water, less so in spirit, insoluble in ether and chloroform, and does not contain nitrogen. Its composition appears to be $C_{29}H_{14}O_{14}$. All the mineral and some of the organic acids decompose strophanthin into glucose and *strophanthidin*, which crystallises readily from a 1·5 per cent. solution of sulphuric acid, but a further decomposition, accompanied with formation of glucose, appears to be produced when the solution of strophanthin in 1·5 per cent. sulphuric acid is boiled for four hours; 4·3 per cent. of a brown, amorphous compound being formed. From this it would seem that an acid is not the best substance to produce strophanthidin from strophanthin, and it is probable that Hardy and Gallois' strophanthin was strophanthidin. A long account of reactions is also given. E. W. P.

Unorganised Ferments. By O. Loew (*J. pr. Chem.* [2], **37**, 101—104).—The author, whilst admitting that in the preparation of diastase by precipitation with lead acetate a product is obtained which is slightly impure owing to the presence of dextrin-like substances, denies that the diastase loses its activity (see Abstr., 1887, 165). If the compound analysed by Lintner is not a mixture, a difference must exist between animal and vegetable diastase, the former being an albuminoïd, the latter an albuminoïd combined with some other substance.

When 0·1 gram of diastase, possessing great activity, but still containing dextrin-like substances, was placed in a dilute solution containing 0·15 gram of hydroxylamine, it was rendered completely inactive at the end of 24 hours. Diastase is also readily rendered inactive by relatively small quantities of nitrous acid at 40°. Pepsin and diastase both lose their activity when allowed to remain in contact with a dilute solution of formaldehyde (1 gram of ferment, 10 grams water, and 5 c.c. of a 15 per cent. solution of formaldehyde) for one day. Some ferments, emulsin, papayotin, trypsin, and other albuminoïds give with formaldehyde precipitates soluble with difficulty in alkalis and acids. Perhaps the loss of activity which the unorganised ferments suffer in presence of acids and alkalis by warming to 80° and under other influences, is due to isomeric change in the amido- and aldehyde-groups contained in the ferments.

G. T. M.

New Parvoline (Dimethylethylpyridine). By E. Dürkopf and M. Schlaugk (*Ber.*, **21**, 832—836).—*Dimethylethylpyridine*,

$$C_5NH_2Me_2Et,$$

is prepared by heating propaldehydeammonia (1 mol.) and paraldehyde (= 3 mol. C_2H_4O) in sealed tubes for 10 hours at 210°. The reddish-brown, oily mass obtained is distilled with steam, the aqueous distillate strongly acidified with hydrochloric acid, evaporated, the hydrochlorides decomposed with potash and fractionally distilled. The fraction 180—200° of the bases is then converted into the mercurochlorides; by this means, as the new parvoline mercurochloride is nearly insoluble in cold water, a separation from collidine and other bases of lower boiling point is readily effected. It is a clear, colourless, strongly refractive, mobile liquid of mild, agreeable, sweetish odour, boils at 188°, has sp. gr. 0·94185 at 0°, 0·92894 at 16° (water at 4° = 1). It is less soluble in hot than in cold water. The *mercurochloride*, $C_9NH_{13},HCl,3HgCl_2$, forms long, lustrous, pure white, spear-shaped needles, or small, well-formed tables of rhombic habit, and melts at 116°. The *platinochloride*, $(C_9NH_{13})_2,H_2PtCl_6$, crystallises in large, tabular, triclinic forms. The *aurochloride* forms lustrous, citron-yellow needles or thin plates, and melts at 86—87°. The *picrate* melts at 152°.

Methylpyridinedicarboxylic acid, $C_5NH_2Me(COOH)_2$, prepared by the oxidation of the parvoline with a 2 per cent. solution of potassium permanganate, crystallises in small, thin, rhombic plates, melts at 225°, and is sparingly soluble in hot water. By the further oxidation of the parvoline, a *pyridinetricarboxylic* acid, $C_5NH_2(COOH)_3$, was obtained, which forms hard, globular, crystal aggregates, melts at 318·7° (corr.) with intumescence, and is readily soluble in hot water. It gives a blood-red coloration with ferrous sulphate, a yellow coloration with ferric sulphate, a blue, crystalline precipitate with copper sulphate. Although all six possible pyridinetricarboxylic acids are known, it has not yet been possible to identify this acid with certainty with any one of them. It closely resembles Weber's carbodinicotinic acid (Abstr., 1887, 1118) in its whole behaviour, but that is described as melting at 223° and crystallising with 1½ mol. H_2O.

A. J. G.

α-Stilbazole (α-Cinnamylpyridine) and its Reduction Products. By H. Baurath (*Ber.*, 21, 818—825; compare this vol., p. 65).—The author has changed the name of this substance from α-cinnamylpyridine to *α-stilbazole*. It boils at 324—325° (corr.) under 750 mm. pressure; its alcoholic solution is without action on litmus. The *hydrochloride*, $C_{13}H_{11}N,HCl + 4H_2O$, crystallises in concentrically grouped needles, and when anhydrous melts at 177°. The *platinochloride*, $(C_{13}H_{11}N)_2,H_2PtCl_6 + 2H_2O$, forms small, reddish-yellow needles which begin to melt with slight evolution of gas at 181°, and are completely fused at 188° without carbonisation. The *aurochloride*, $C_{13}H_{11}N,HAuCl_4$, forms sparingly soluble, cinnabar-red crystals, and melts at 185°. The *mercurochloride*, $C_{13}H_{11}N,HHgCl_3 + H_2O$, melts at 181—183°. The *periodide*, $C_{13}H_{11}N,HI,I_2$, crystallises in prisms of bluish lustre, which in very thin layers transmit reddish-violet light. When oxidised, stilbazole yields benzoic and picolinic acids.

Dihydro-α-stilbazole, $C_5NH_4{\cdot}CH_2{\cdot}CH_2Ph$ [CH_2 = 2], is prepared by heating stilbazole with five times the quantity of fuming hydriodic acid for one hour, the new compound separating as its periodide. It is liquid at ordinary temperatures, but can be solidified by long exposure to a low temperature, and then melts at −3°; it boils at 289·5° (corr.) under 766 mm. pressure, has a sweet, agreeable odour, is sparingly soluble in water, miscible in all proportions with alcohol, ether, and benzene, and volatilises with steam. Sp. gr. at 0° = 1·0465 (water at 4° = 1). The *hydrochloride* and *sulphate* crystallise in small needles; the *platinochloride*, $(C_{13}H_{13}N)_2,H_2PtCl_6$, forms small, reddish-yellow needles, and melts at 185—186°; the *aurochloride*,

$$C_{13}H_{13}N,HAuCl_4,$$

is the most characteristic salt; it forms lustrous, yellow needles several cm. long, sinters at 145°, and melts at 149—150°; the *mercurochloride*, $C_{13}H_{13}N,HHgCl_3$, is sparingly soluble, and melts at 149°.

α-Stilbazoline, $C_5NH_{10}\cdot CH_2\cdot CH_2Ph$, is prepared by adding sodium to a hot solution of α-stilbazole in absolute alcohol, decomposing the product with water, acidifying, distilling off the alcohol, and concentrating the aqueous solution on the water-bath; a considerable amount of liquid hydrocarbons formed as bye-products in the reaction have to be removed by aid of a separating funnel. The concentrated solution is then slightly acidified and treated with sodium nitrite in the warm for some time, when the nitroso-derivative of stilbazoline separates in large, reddish drops; this is extracted with ether and the ether distilled off. As the nitrosamine cannot be distilled, it is decomposed with hydrogen chloride, the reaction, at first very violent, being moderated by cooling, but later on assisted by heating. The product is largely diluted, extracted several times with ether to remove any unaltered nitrosamine, and the base finally liberated by treatment with alkali. It is a slightly oily liquid, does not solidify in a mixture of carbonic anhydride and ether, boils at 288° (corr.) under 760 mm. pressure, has sp. gr. 0·9874 at 0° (water at 4° = 1), and is sparingly soluble in water, miscible in all proportions with alcohol, ether, and benzene. Litmus-paper is not affected by the dry base, but in presence of water is turned blue. The *hydrochloride*, $C_{13}H_{19}N,HCl$, forms slender, colourless needles, and melts at 155°; the *platinochloride*, $(C_{13}H_{19}N)_2,H_2PtCl_6$, melts at 187—189°, and begins to decompose at 190°; the *aurochloride* melts at 133—134°; the *mercurochloride* and *periodide* were only obtained as oils. Stilbazoline resembles conine in its physiological action, but is less active, the lethal doses per 1 kilo. body-weight being 0·07578 for conine and 0·09614 for α-stilbazoline.

The difference in the atomic volumes of dihydro-α-stilbazole and α-stilbazoline corresponds with a value of 5·5 for H_2, a number agreeing approximately with that obtained by Horstmann (Abstr., 1887, 546) in the pyridine series. A. J. G.

Molecular Migrations in the Quinoline Series. By J. ZIEGLER (*Ber.*, **21**, 862—867).—*Paramidotetrahydroquinoline*, $C_9NH_{10}\cdot NH_2$, is prepared by reducing Fischer and Hepp's tetrahydronitrosoquinoline (Abstr., 1887, 729) with tin and hydrochloric acid; it forms strongly refractive, transparent, rhombic crystals, melts at 97°, can be distilled unchanged under reduced pressure, and is soluble in ether and benzene. The aqueous solution gives a violet coloration with ferric chloride, which on addition of hydrochloric acid changes to emerald-green. The same substance is obtained by reduction of La Coste's paramidoquinoline with tin and hydrochloric acid. The *hydrochloride*, $C_9N_2H_{12}.2HCl$, forms snow-white, hygroscopic needles, and melts at 244—246°; the *platinochloride*, $C_9H_{12}N_2,H_2PtCl_6$, is a yellow, crystalline powder; the *picrate* forms satiny, siskin-green crystals melting at 176°; the *oxalate* melts at 168°. The *diacetyl*-compound, $C_9H_{12}N_2Ac_2$, crystallises in concentrically-grouped white needles, and melts at 172°.

In addition to the method given by La Coste (Abstr., 1883, 811), paramidoquinoline can be prepared by converting sulphanilic acid into paraquinolinesulphonic acid by Skraup's method, converting this into parahydroxyquinoline by fusion with potash, and heating the latter with ammonio-zinc chloride for 10 hours at 270—280°.

When paramidoquinoline is dissolved in methyl alcohol and heated with excess of methyl iodide in a reflux apparatus for some hours, it is converted into *dimethamidomethylhydroquinoline dimethiodide*,

$$C_9NH_9Me\cdot NMe_2,2MeI;$$

this forms nearly white crystals melting at 171°.

Paradinitrosotetrahydroquinoline, $C_9H_9N_3O_2$, is prepared by treating an acetic acid solution of paranitrosohydroquinoline with the calculated quantity of sodium nitrite; it forms long, moss-green needles, melts at 98°, and explodes at a slightly higher temperature; it gives Liebermann's reaction.

When solutions of paranitrosohydroquinoline and phenylhydrazine are mixed, a substance crystallising in lustrous, yellow plates is obtained; it melts at 126° with explosion.

When toluquinoline prepared from orthotoluidine is hydrogenised and converted into the corresponding nitroso-compound, a heavy, yellowish oil is obtained. When this is dissolved in an equal quantity of absolute alcohol and as much again alcoholic hydrogen chloride added, there separates after some hours the hydrochloride of the isomeric nitroso-compound. By treatment with ammonia, the free base $C_{10}H_{12}N_2O$ is obtained, and after crystallisation from benzene forms steel-blue crystals of metallic lustre which melt at 140°. When reduced, it yields a paramidotoluhydroquinoline, whose aqueous solution gives with ferric chloride the characteristic red coloration, turning emerald-green on addition of hydrochloric acid; the *hydrochloride*, $C_{10}H_{16}N_2Cl_2$, melts at 166°.

Paranitrosotetrahydroquinoline is converted into paramidoquinoline under certain conditions; this change occurs very slowly if the substance is moistened with hydrochloric acid and left to itself, or if the hydrochloride is heated at 105°, but it is most complete if an aqueous solution of the hydrochloride is left for some days in the warm or is heated in a reflux apparatus for a few hours. A. J. G.

Orthohydroxyquinaldinecarboxylic Acid. By W. König (*Ber.*, 21, 883—884).—*Orthohydroxyquinaldinecarboxylic acid*,

$$OH\cdot C_9NH_4Me\cdot COOH,$$

is prepared by heating the potassium compound of orthohydroxquinaldine with liquid carbonic anhydride in an autoclave for six to seven hours at 180—190°. It crystallises with 1 mol. H_2O in long, golden-yellow needles, becomes anhydrous at 120°, and melts at 207° with decomposition into orthohydroxyquinaldine and carbonic anhydride. It is sparingly soluble in cold, more soluble in hot water or alcohol, insoluble in ether. The aqueous solution gives a cherry-red coloration with ferric chloride. A. J. G.

Sparteïne. By F. B. AHRENS (*Ber.*, **21**, 825—832).—As the reduction and oxidation of sparteïne (Abstr., 1887, 1056) threw no light on its constitution, it seemed necessary to have recourse to more energetic reactions in order to investigate this question.

When sparteïne is heated with seven to eight times its weight of 57 per cent. hydriodic acid for five hours in sealed tubes at 200°, it yields methyl iodide and a new base, $C_{14}H_{24}N_2$, which distils at about 276°, and has a strong, peculiar odour. Its platinochloride forms small, yellowish-red crystals, and blackens and decomposes at 230°; the aurochloride melts at 157°. As it readily yields a nitroso-compound, it must be a secondary base, and it follows that the eliminated methyl-group must have been united to nitrogen.

When sparteïne is distilled with five times its weight of lime, it yields ethylene, propylene, γ-picoline, and a very small quantity of a tertiary base that could not be identified with certainty, whilst when passed through tubes heated to dull redness, pyridine, γ-picoline, a small quantity of a secondary base, ethylene, propylene, non-aromatic hydrocarbons, ammonia, and hydrogen cyanide are obtained. The aurochloride of the secondary base melts at 172°.

From these investigations the author considers it probable that the sparteïne molecule contains two pyridine-rings, and that these are hydrogenised, seeing that pyridinecarboxylic acids cannot be obtained on oxidation (*loc. cit.*), nor can more than two hydrogen-atoms be taken up. With regard to the side-chains, there is one methyl-group attached to nitrogen and another united to one pyridine-ring at the γ-position, and probably also there is a side-chain of three carbon-atoms. A. J. G.

Optical Rotatory Power of Papaverine. By G. GOLDSCHMIEDT *Monatsh.*, **9**, 42—44).—Several observations made with pure papaverine show that the compound is inactive. The results confirm the correctness of the Bel-Van't Hoff theory, and at the same time give important support to the author's papaverine formula (Abstr., 1886, 478). As papaverine and laudanine were hitherto the only exceptions to the rule that derivatives of active substances are also active, and as papaverine is shown in the present paper to form no exception, it is suggested that a renewed examination of laudanine is desirable (compare Hesse, *Annalen*, **176**, 198). N. H. M.

Narceïne. By A. CLAUS and A. MEIXNER (*J. pr. Chem.* [2], **37**, 1—9).—In a previous paper (Abstr., 1885, 996), one of the authors describes a substance obtained by treating commercial narceïne with potassium permanganate. This proves to be pure narceïne; it melts at 162° (uncorr.). The platinochloride $(C_{23}H_{29}NO_9)_2,H_2PtCl_6$, crystallises in golden-yellow needles, melting at 195° (uncorr.).

On oxidising narceïne (1 mol.) with potassium permanganate ($4\frac{1}{2}$ mols.), *narceinic acid*, $C_{15}H_{15}NO_8 + 3H_2O$, is formed. It crystallises from hot water in forms belonging to the rhombic or monoclinic system. The trisodium salt, $C_{15}H_{12}NO_8Na_3$, dissolves readily in water, from which it is precipitated by alcohol. The disodium salt, $C_{15}H_{13}NO_8Na_2 + 5H_2O$, crystallises from water in small, colourless needles, melting at 85° (uncorr.). The monosodium salt, $C_{15}H_{14}NO_8Na + 4\frac{1}{2}H_2O$, also crystallises in small needles, and dissolves readily in water. The barium salt, $(C_{15}H_{12}NO_8)_2Ba_3 + 5H_2O$, is fairly soluble in water. At 180—200°, narceinic acid yields carbonic anhydride, dimethylamine, and a *dihydroxynaphthalenedicarboxylic acid*,

$$C_{10}H_4(OH)_2(COOH)_2,$$

which is best purified by sublimation, and crystallises in long needles, melting at 162° (uncorr.). It dissolves readily in ether and chloroform, but is almost insoluble in water and alcohol. Both the normal sodium salt, $C_{12}H_6O_6Na_2 + 6OH_2$, and the acid salt, $C_{12}H_7O_6Na + 5\frac{1}{2}H_2O$, crystallise in small, colourless needles. On reduction with hydriodic acid, a naphthalenedicarboxylic acid is formed, melting at 250—253°, and seeming to agree in properties with the γ-naphthalenedicarboxylic acid described by Wichelhaus and Darmstädter (*Annalen*, **152**, 309). G. T. M.

Cinchonigine. By E. JUNGFLEISCH and E. LÉGER (*Compt. rend.*, **106**, 357—360).—*Cinchonigine*, $C_{19}H_{22}N_2O$, is obtained by heating the hydrochloride (this vol., p. 380 and 507) with soda and extracting with ether. When the ether is distilled off, an oily residue is left, which in contact with dry air gradually changes to a colourless, crystalline mass. If recrystallised from anhydrous ether, cinchonigine forms short, bulky, highly refractive, colourless prisms, which melt at 128°. It distils regularly under reduced pressure. In a 1 per cent. solution in alcohol of 97°, the rotatory power $[\alpha]_D = -60{\cdot}1°$; in a solution of half the strength, $[\alpha]_D = -61{\cdot}16°$. In a 1 per cent. solution in hydrochloric acid containing 2 mols. of the acid to each molecule of base, $[\alpha]_D = -40{\cdot}70°$; with twice the proportion of acid $[\alpha]_D = -38{\cdot}21°$.

Cinchonigine is slightly soluble in water, and is alkaline to litmus, but neutral to phenolphthaleïn. It is very soluble in methyl, ethyl, and amyl alcohols, chloroform, benzene, and acetone, but is less soluble in anhydrous ether. The acid solutions are not fluorescent. Cinchonigine yields the same products of decomposition as cinchonine.

Cinchonigine forms basic salts which are feebly alkaline to litmus, and normal salts which have an acid reaction and are usually crystalline, stable, and soluble in water. The *basic hydrochloride*,

$$C_{19}H_{22}N_2O,HCl + H_2O,$$

forms large, colourless, highly refractive, prismatic needles, which melt at 213°, and decompose without volatilising. It is only slightly soluble in cold water but dissolves more readily at 100°. In a 1 per cent. aqueous solution, the rotatory power $[\alpha]_D = -65{\cdot}41°$. The *platinochloride*, $C_{19}H_{22}N_2O,H_2PtCl_6 + H_2O$, forms small, bright-orange prisms only slightly soluble in warm water. The *basic hydrobromide*, analogous in composition to the chloride, crystallises from boiling water in short, slightly efflorescent prisms, which melt at 218·5°, and are only slightly soluble in cold water. The *basic hydriodide* crystallises in non-efflorescent, prismatic needles, which melt at 223°. The *normal hydriodide*, $C_{19}H_{22}N_2O,2HI + H_2O$, is obtained by cooling a solution of the preceding compound mixed with hydriodic acid. It forms bright-yellow crystals, which are only slightly soluble in water, and are decomposed by light, with liberation of iodine. The *normal dextrotartrate* crystallises with 7 mols. H_2O in long, prismatic needles. It is much less soluble than the basic tartrate. The *basic oxalate* forms needles, which if left in the mother-liquor change to large, efflorescent, very soluble tables, containing 5 mols. H_2O. The same crystals are obtained by spontaneous evaporation of the solution. The *basic chromate* is crystalline; the *basic sulphate* forms highly soluble needles; the *thiocyanate* is crystalline and only slightly soluble, and unites with zinc thiocyanate to form a bulky, amorphous, colourless, insoluble compound; the *aurochloride* is pale-yellow and amorphous.

Cinchonigine methiodide, $C_{19}H_{22}N_2O,MeI$, obtained by mixing ethereal solutions of cinchonigine and methyl iodide, crystallises from alcohol in colourless, anhydrous needles, which melt with decomposition at 253°. It is slightly soluble in water or cold alcohol, very soluble in chloroform, acetone, and amyl alcohol; insoluble in ether or benzene. Methyl chloride forms an analogous compound.

Cinchonigine ethiodide, obtained in a similar manner, forms large, lemon-yellow prisms, which contain $2H_2O$. It melts at 232°, with slight decomposition, and is more soluble than the methyl-derivative in alcohol or water. Ethyl bromide forms a similar compound, which melts at 217° with decomposition, and is very soluble in water, chloroform, ethyl alcohol, and acetone, but is insoluble in ether or benzene.

C. H. B.

Colchicine. By S. ZEISEL (*Monatsh.*, 9, 1—30; compare Abstr., 1887, 284).—Determinations of methoxyl (Abstr., 1886, 493 and 1079), in colchicine and colchiceïne, showed that the former contains four, and the latter three methoxyl-groups.

When colchiceïne is heated on a water-bath with hydrochloric acid, acetic acid distils, and a mixture of the hydrochlorides of trimethylcolchicine, dimethylcolchicinic and colchinic acids are obtained. The residue is diluted with a little water, and extracted with chloroform, which takes up only the first mentioned of the three hydrochlorides.

Trimethylcolchicinic acid, $COOH{\cdot}C_{15}H_9(OMe)_3{\cdot}NH_2$, is obtained by precipitating the hot aqueous solution of the hydrochloride with the exact amount of potash; it forms microscopic prisms, with 2 mols. H_2O, melts at 159°, and decomposes when heated for a long time at 150°. The *hydrochloride* forms lustrous, yellowish-white plates, moderately soluble in cold water, with bright-yellow colour; the aqueous solution reddens litmus. In its general behaviour to alkaloïd reagents, it resembles colchiceïne hydrochloride. The *platinochloride*,

$$(C_{19}H_{21}NO_5)_2,H_2PtCl_6 + 2H_2O,$$

crystallises in groups of yellow needles.

Dimethylcolchinic acid, $COOH{\cdot}C_{15}H_9(OMe)_2(OH){\cdot}NH_2$, is prepared by precipitating a 2 per cent. solution of the hydrochloride with the necessary amount of aqueous soda; the crystals (with 4½ mols. H_2O) melt at 141—142°. The *hydrochloride* (with 1 mol. H_2O) is rather sparingly soluble in water and alcohol.

Colchicinic acid, $COOH{\cdot}C_{15}H_9(OH)_3{\cdot}NH_2$, was not obtained quite pure, or in a crystalline form. The dilute hydrochloric acid solution gives an intense brownish-red coloration with ferric chloride.

Acetotrimethylcolchicinamide, $NHAc{\cdot}C_{15}H_9(OMe)_3{\cdot}CONH_2$, is formed when 10·5 grams of colchicine is heated with 15 c.c. of 5 per cent. alcoholic ammonia for four hours at 100°. A reaction seems to take place in the cold, as the mixture becomes red after some hours, or greenish when seen in thin layers. The liquid shows a characteristic absorption spectrum; this disappears after the solution has been heated for four hours at 100°. The amide is crystallised from hot alcohol, from which it separates in two forms, of which the one crystallises in the rhombic system, with 1 mol. EtOH. It is readily soluble in dilute hydrochloric acid; almost insoluble in water. When the alcoholic solution is heated with aqueous soda at 110°, colchiceïne is formed. The *hydrochloride*, *platinochloride*, and *aurochloride* were prepared. The solution of the base in dilute alcohol gives an intense brown coloration with ferric chloride. When the strong hydrochloric acid solution of the amide is treated with a small amount of potassium nitrite, it acquires a splendid violet colour. Several other reactions are described.

N. H. M.

Compounds of Gelatin with Tannin. By C. Böttinger (*Annalen*, **244**, 227—232).—The precipitate produced by gelatin in a solution of tannin contains 16·5 per cent. of nitrogen, corresponding with 34 per cent. of tannin. The precipitate is decomposed by water at 150°, yielding a solution which gives an abundant precipitate with tannin.

The precipitate produced by gelatin in a solution of oak-bark tannin contains 9·5 per cent. of nitrogen, corresponding with 42·7 per cent. of tannin. It is decomposed by water at 150°, yielding three products, which are respectively freely soluble in cold water, soluble in hot, and insoluble in water.

Hide tanned with oak-bark behaves in a similar way. The portion insoluble in water slowly dissolves in alkalis and alkaline carbonates.

W. C. W.

Urohæmatoporphyrin and Allied Pigments. By C. A. MacMunn (*Proc. Physiol. Soc.*, 1888, 5—6).—In the study of urinary pigments, it is necessary to pay attention to certain feeble bands in the red half of the spectrum which have been overlooked by many previous observers. The following reagents, ammonia, ammonio-zinc chloride, zinc chloride alone, and aqueous soda, cause characteristic changes in urinary pigments. From a study of these changes, the following conclusions are drawn:—(1.) Two entirely distinct substances have been included by physiologists under the name urobilin, namely, that of normal and that of pathological urine. (2.) Hydrobilirubin is not identical with either. (3.) Normal urobilin is identical with a pigment produced by the action of peroxide of hydrogen on acid hæmatin, and subsequent brief reduction with sodium amalgam; pathological urobilin cannot as yet be traced definitely to its source, but it is very closely related to normal urobilin. (4.) Hydrobilirubin and human stercobilin are not identical; but in the cat the pigment of the fæces appears to be hydrobilirubin. (5.) Stercobilin and pathological urobilin appear to be closely connected; both are probably derived from hæmatin, and not directly from biliary pigments. (6.) Urohæmatoporphyrin (called by le Nobel isohæmatoporphyrin, see Abstr., 1887, 1127) is beyond doubt a reduction product of hæmatin, and the urobilinoidin of le Nobel is its chromogen; this chromogen is sometimes present in pathological urine. Urohæmatoporphyrin has been found in the urine of patients suffering from rheumatism, pericarditis, Addison's disease, cirrhosis of the liver, croupous pneumonia, Hodgkin's disease, measles, typhoid fever, and meningitis. The band at F in the spectrum of this substance is not removed by ammonia; in this it resembles stercobilin, but differs from urobilin and from hydrobilirubin.

W. D. H.

Physiological Chemistry.

Influence of Diet on the Elimination and Absorption of Carbon. By M. Hanriot and C. Richet (*Compt. rend.*, **106**, 419—422).—An account of experiments on the products of respiration of a man existing on a mixed diet of nitrogenous, fatty, and amylaceous food. The influence of each ingredient in the diet will be determined by subsequent experiments. The ratio of oxygen absorbed to carbonic anhydride produced remains constant under constant conditions, hence it would seem that respiration is regulated automatically. During digestion the ratio rises, that is to say there is an increased absorption of oxygen.

C. H. B.

Influence of Diet on Respiratory Changes. By M. Hanriot and C. Richet (*Compt. rend.*, **106**, 496—498).—This paper contains details of experiments which show that respiration is increased by taking food, but almost solely when the food consists of carbohydrates. Nitrogenous and fatty foods have little effect on the respiratory process. Amylaceous food increases the volume of air respired and the quantity of oxygen absorbed, but its effect is most strongly marked in the increased production of carbonic anhydride. The percentage proportion of oxygen absorbed and carbonic anhydride produced varies but little during repose. The oxygen absorbed amounts on an average to 4·2 per cent. of the air inspired, with variations between 3·4 and 4·7, whilst the quantity of carbonic anhydride produced is on an average 3·4 per cent. of the air expired, with variations between 2·7 and 4·2. A healthy adult man inspires 8 litres of air per hour per kilogram of body-weight, with formation of 0·5 gram of carbonic anhydride and absorption of 0·45 gram of oxygen. During digestion, the volume of air inspired increases to 9 litres per kilogram per hour, with formation of 0·6 gram of carbonic anhydride and absorption of 0·5 gram of oxygen.

C. H. B.

Volatile Bases in the Blood and Breath. By R. WURTZ (*Compt. rend.*, **106**, 213—214).—The air expired from the lungs was passed into a 1 per cent. solution of oxalic acid, care being taken to prevent the introduction of saliva or solid particles. When several cubic metres had been passed through, the liquid was neutralised with calcium carbonate, mixed with a few drops of lime-water, filtered, exactly neutralised with hydrochloric acid, and evaporated in a vacuum. Ammonium chloride is the chief product, but is mixed with the hydrochloride of an organic base which gives precipitates with Bouchardat's reagent and mercuric potassium iodide. It forms a soluble aurochloride, and a soluble platinochloride which crystallises in short needles and seems to be identical with the platinochloride of a volatile base obtained from the blood. A solution of the hydrochloride heated at 100° has a peculiar and characteristic odour. C. H. B.

Action of Acids on the Functional Activity of the Human Stomach and their Therapeutical Application. By W. JAWORSKI (*Chem. Centr.*, 1887, 1560—1561, from *D. Med. W.*, **13**, 792—796). —The results of the investigation of the action of hydrochloric, lactic, acetic and carbonic acids are as follows:—(1.) The mucus is precipitated in the stomach by the acids. (2.) Cell nuclei appear in the stomach contents, especially after the introduction of hydrochloric acid. (3.) The stomach contents show an increased biuret reaction, again most marked after hydrochloric acid. (4.) Large doses of acid usually cause an inflow of bile into the stomach. (5.) The secretion of pepsin is assisted materially by acids, whilst the secretion of hydrochloric acid is only very slightly influenced, or not more so than it would be by the introduction of distilled water. (6.) 200 c.c. of normal acid disappear from the stomach in 1¼ to 1½ hours. (7.) After long-continued consumption of acid, the secretion of hydrochloric acid was checked. (8.) With large quantities of hydrochloric acid, the subjective stomach symptoms do not appear, or only in a slight degree. (9.) The difference between the action of acids and salts of the alkalis on the digestive function of the stomach is that alkalis dissolve mucus and hinder secretion of pepsin, whereas acids precipitate the mucus and induce the secretion of pepsin. After the disappearance of alkalis from the stomach, an increased secretion of hydrochloric acid follows, but after the disappearance of acids there is none, or only a slight secretion.

Both agree in this, that after long use in large quantities they check the secretion of hydrochloric acid or cause it to cease.

In mucous catarrh of the stomach which accompanies in most cases carcinoma of the stomach, the acidity and the secretion of pepsin are probably reduced by the action of the mucus. In pathological cases of this kind, a larger quantity of hydrochloric acid should be used for therapeutical purposes. The author supplements his previous statements respecting carbonic anhydride. Carbonic anhydride both as a gas and dissolved in water favours the secretion of hydrochloric acid (in contradistinction to the above-mentioned acids) and pepsin and consequently the digestive power of the gastric juice. It assists also in increasing the mechanical activity of the stomach.

The concluding part of the paper contains remarks on the clinical use of the acids. J. P. L.

Amount of Acid in the Stomach on an Amylaceous Diet. By J. Rosenheim (*Chem. Centr.*, 1887, 1561, from *Med. Centr.*, **25**, 865—866).—In healthy subjects, after ingestion of 50 grams of wheaten bread and 150 c.c. of water, the following results were obtained:—(1.) 15 minutes after the commencement of the experiment 0·3 part in 1000 of free hydrochloric acid was present, the quantity quickly increased to 1 part in 1000 after 30 minutes; at which point it remained constant until the complete elimination of the chyme from the stomach. (2.) Lactic acid is present throughout in moderately uniform amount. (3.) Volatile acids are always present although only in traces. In pathological conditions, the free hydrochloric acid present 15 minutes after the commencement of the experiment varies from 0·1 in 1000 in carcinoma to 1 in 1000 in abnormal acidity. After ingestion of pure carbohydrates on an empty stomach, the free hydrochloric acid both in normal and pathological cases was sensibly less than in the previous experiment. Only 0·2 part of hydrochloric and 0·2 part of lactic acid in 1000 were found after one hour's digestion.

Finally, if boiled starch is introduced into the stomach with careful exclusion of saliva, large quantities of hydrochloric acid and an approximately equal amount of lactic acid were always found.

J. P. L.

Free Hydrochloric Acid in the Stomach Contents. By A. Günzburg (*Chem. Centr.*, 1887, 1560, from *Med. Centr.*, **40**).—The method depends on the phloroglucinol-vanillin test of Wiesner and Singer, which gives a red colour with hydrochloric acid. The reagent consists of 2 parts of phloroglucinol, 1 part of vanillin, and 30 parts of rectified spirit. A few drops of the filtered gastric juice is mixed with a like quantity of the reagent and carefully evaporated in a small capsule, red crystals or, if much organic matter (especially peptone) be present, a red paste is formed. The reaction takes place with 1 part hydrochloric acid in 10,000, but not with 1 in 20,000.

In many cases in consequence of acid albuminates, there is no reaction. For quantitative estimations, the reaction is not of much value, although an approximation can be obtained by diluting the original gastric juice gradually with successive known quantities of water until the limit of reaction 1 in 20,000 is attained. J. P. L.

Does Cellulose Economise the Decomposition of Proteïd in the Nutrition of Herbivora? By H. Weiske (*Zeit. Biol.*, **24**, 553—561).—v. Knierem (this vol., p. 515) has recently again disputed the conclusions arrived at by Weiske and others on this subject. The present paper is a reply to his recent criticisms, and in it the author again affirms that cellulose does not economise the decomposition of proteïd, and also points out that v. Knierem's own experiments may be so interpreted as to support this statement.

W. D. H.

Changes Effected by Digestion on Fibrinogen and Fibrin. L. C. Wooldridge (*Proc. Roy. Soc.*, **43**, 367—368).—Fibrinogen is a name conveniently given to a group of proteïds which can be converted into fibrin, which exist in blood plasma, and can be obtained from almost all animal tissues. They are all extremely easily changed by precipitation, are soluble in water (as caseïn is dissolved in milk), and are readily precipitated by acetic acid and dilute mineral acids in excess, but soluble in greater excess. On adding pepsin to the acid solutions, a precipitate appears in the course of a few hours, which is soluble in dilute alkalis, and on incineration leaves an acid ash which is rich in phosphorus. The phosphorus is stated to be present in the form of lecithin. The ash also contains iron. The fibrin which is formed from these fibrinogens is stated also to contain lecithin, but is entirely soluble in artificial gastric juice. Ordinary fibrin obtained by whipping blood always leaves an undigested residue, due partly to the presence of admixed white corpuscles (Hammarsten), partly, however, to its containing unchanged fibrinogen. W. D. H.

Influence of Bile on Digestion. By S. H. C. Martin and D. Williams (*Proc. Physiol. Soc.*, 1888, 1).—In artificial digestion experiments, it was found that bile acids very considerably accelerated the amylolytic action of the pancreatic juice. Varying percentages of pig's bile in a solution of starch (2 per cent.) were used, and glycerol extract of pig's pancreas added. A control experiment was always made with bile and starch alone. It was found that the iodine reaction of starch disappeared more rapidly from the solution containing bile and pancreatic extract than from that containing pancreatic extract alone, and that the rapidity of disappearance was proportionate to the amount of bile present up to 4 per cent., beyond which experiments were not performed. W. D. H.

Influence of Bile on the Digestion of Fats. By A. Dastre (*Compt. rend.*, **106**, 217—220).—It is known that in the rabbit the pancreatic juice alone is not sufficient to effect the digestion of fats. The author's experiments on dogs by means of a cholecysto-intestinal fistula, produced artificially, show that bile alone is equally unable to effect this change. It follows that the simultaneous action of the pancreatic juice and the bile is essential, and it would seem that bile promotes absorption of the fats, whilst the pancreatic juice is an active agent in their decomposition. C. H. B.

Stability of Carbonic Oxide and Oxalic Acid in the Animal Organism. By G. GAGLIO (*Chem. Centr.*, 1887, 1514 (from *Arch. exp. Path.*, **22**, 235).—From the results of a series of respiration experiments, the author shows that carbonic oxide undergoes no oxidation when respired. He also states in opposition to Porkowsky that carbonic oxide is not oxidised by blood outside the body.

Oxalic acid dissolved in pig's blood and circulated through pig's kidneys for several hours only showed a loss of 7 per cent., a loss which occurred when oxalic acid was simply added to the kidney without circulation.

The same result was obtained in feeding experiments, the whole of the oxalic acid, with the exception of 7 to 9 per cent., being recovered from the urine. J. P. L.

Coagulation of the Blood. L. C. WOOLDRIDGE (*Zeit. Biol.*, **24**, 562—563).—In reply to the criticisms of Krüger (this vol., p. 305) Wooldridge states that he has never questioned the fact that leucocytes bring about coagulation in extravascular plasma, but he again states that as soon as they are introduced into the circulating blood they lose this property. W. D. H.

Chromatology of Sponges. C. A. MACMUNN (*Journ. Physiol.*, **9**, 1—25).—Out of the 12 species of British sponges examined, 10 (enumerated) were found to contain chlorophyll; Krukenberg and other observers have figured the dominant chlorophyll band in eight others. Probably Krukenberg (*Grundzüge einer vergleich. Physiol. der Farbstoffe*, 1884) used solutions which were too dilute to show the remaining bands, or examined only thin layers of the solutions. Lipochromes occur in nearly all sponges, and a histohæmatin in seven of the sponges examined. A pigment resembling a floridine (a class of red pigments described by Krukenberg) occurs in *Halichondria rosea*, in addition to chlorophyll, a histohæmatin, and a lipochrome. A uranidine (a class of yellow pigments described by Krukenberg) occurs in *Grantia coriacea*, in addition to chlorophyll and a lipochrome. This uranidine, like Krukenberg's aplysinofulvin (one of the five pigments of Aplysina), and others of the same class was changed by boiling to dark-green. With regard to the chlorophyll present in so many sponges, it was found to resemble plant chlorophyll very closely. The lipochrome constituent or constituents, however, reacted differently from the lipochrome constituents of plant chlorophyll, as it remained unchanged by the action of iodine in iodide of potassium, and the fractional method did not separate the chlorophyll constituents (Hansen's "chlorophyll-green" and "chlorophyll-yellow") so completely as in the case of plant chlorophyll. In these two points, it resembles enterochlorophyll (MacMunn, Abstr., 1885, 1242), and proves that the chlorophyll is of purely animal origin. Microscopic search for unicellular algæ, moreover, yielded negative results. The fact that in sponges lipochromes so often accompany chlorophyll, and sometimes replace it, would go to show that the step from a lipochrome to a chlorophyll is not a great one; and it is highly probable that these pigments are concerned in the formation of fatty matters perhaps from the waste carbonic anhydride given off during the katabolic changes in the tissues, and from the water in which they are bathed; carbohydrates are perhaps similarly formed. This would coincide with the views of Schunck (*Brit. Assoc. Rep.*, 1887), who regards chlorophyll as a respiratory pigment, but probably a carbonic acid-carrier, not an oxygen-carrier. In sponges, the histohæmatin, when present, has probably the function of an oxygen-carrier.

A chart of spectra with measurements accompanies the paper.

W. D. H.

Composition of Cow's Milk. By P. VIETH (*Analyst*, **13**, 46—49).—The analysis of 12,663 samples of milk, taken throughout the year direct from the railway cans upon their arrival at the dairy, showed an average of 3·82 per cent. of fat and 12·94 per cent. of total solids. In addition, 2,948 samples were taken by inspectors during the delivery of the milk to the customers. These gave a general average of 12·89 per cent. of total solids.

An investigation of the changes taking place in the milk during delivery to customers, was made by taking a sample from the can before sending it out, and also one from the small quantity of milk left in the can upon its return from its round. In 17·6 per cent. of the cases, the latter contained more fat (0·1 to 0·34 per cent.) than the former. It is not stated whether the milk was drawn off from the bottom of the can or dipped from the top. M. J. S.

Formation of the Colouring Matter of Bile. By J. LATSCHENBERGER (*Monatsh.*, **9**, 52—92).—Experiments made with horses are described in detail, and give the following results:—The colouring matter of bile is derived from the colouring matter of the blood with simultaneous elimination of a dark pigment containing iron (melanin). The decomposition takes place in the tissues as well as outside the cells. This dissociation of the hæmoglobin into pigments free from iron (choleglobin) and pigments containing iron, occur both in the single blood corpuscles and in the conglomerates; in the former, the rate of decomposition is irregular, which seems to depend on the varying age of the single red corpuscles. With crystallised hæmoglobin there is no difference in time required for the decomposition of single portions of the injected mass.

The results of the microscopic examination of the various preparations are shown in coloured diagrams. N. H. M.

Influence of the Secretion of Gastric Juice on the Quantity of Chlorine in Urine. By G. STICKER (*Chem. Centr.*, 1887, 1561—1562, from *Berl. Klin. W.*, **24**, 768—771).—A rich secretion of gastric juice induces transitorily a diminution of the chlorides in urine, if conditions for its retention in the stomach or its secretion from the organism are given. The hourly secretion of chlorine increases gradually and progressively after the chief meal, and slowly diminishes again after six to seven hours. With the increase of chlorine, the activity of the urine lessens, and even changes into a strongly alkaline reaction. Towards night time, a strong decrease of the secretion of chlorine takes place. From the results of the experiments no direct relation between peptic digestion and secretion of phosphates in urine can be recognised. In urine which showed an alkaline reaction, a turbidity from phosphates was regularly produced after a short time. The mean acidity of the whole 24 hours' urine is no higher on days with paroxysms of excessive acidity than on normal days. J. P. L.

Phosphates in Urine in Different Diseases. By L. VANNI and E. PONS (*Chem. Centr.*, 1887, 1526, from *Ann. Chim. Farm.*, **87**, 259—268).—The authors advance the following conclusion with all reserve:—As a general rule, the amount of phosphate secreted in the urine diminishes in diseases of the brain and spinal cord, and frequently diminishes in cases of neurosis. J. P. L.

Urine Reaction. By ADUCCO (*Arch. Pharm.* [3] **25**, 931, from *Ann. Chim. Farm.*, 1887, 369).—From experiments made on dogs which were compelled to run until exhausted by means of specially constructed apparatus, it was found that as the fatigue increased, the originally acid urine became gradually less acid, neutral and finally alkaline. During rest, the reverse progress went on. The alkaline reaction was caused by the presence of carbonates of the fixed alkalis and of ammonia, the relative amounts of which were, however, not constant. These carbonates are the products of reactions proceeding in the tissues, and it must be concluded that during production of fatigue, such substances more especially are used up as yield carbonic anhydride. The amount of urea present in the urine during the period of fatigue is decidedly less than before or after that period. J. T.

Physiological Action of Alkalis and Alkaline Earths. By CRUCI (*Arch. Pharm.* [3], **25**, 931, from *Ann. Chim. Farm.*, 1887, 353).—Both the alkalis and the alkaline earths increase the blood pressure and the power of the heart, and make the pulse slower but fuller and stronger, hence are stimulants of the circulatory organs. Although the symptoms are uniform, the mechanism affected by the various elements differs considerably. Potassium, rubidium, and cæsium directly affect the muscular apparatus, sodium and magnesium act on the nerve elements, lithium, barium, calcium, and strontium act in both ways. These considerations show that the alkalis and alkaline earths act as stimulants on the circulatory system; this is the more remarkable when it is remembered that the acids in general, and also the oxides of the remaining metals, exert a more or less paralytic action on that system. J. T.

Antiseptic Properties of α-Naphthol. By J. MAXIMOVITCH (*Compt. rend.*, **106**, 366—368).—α-Naphthol is insoluble in cold water, but water at 70° dissolves 0·04 per cent. Alcohol of 40 per cent. dissolves 10 grams of α-naphthol per litre. The quantity required to prevent the development of microbes varies from 0·01 to 0·04 per cent., according to the nature of the microbe and the nidus. α-Naphthol has only one-third the poisonous action of β-naphthol, and only one seven-hundredth of that of mercuric iodide. The fatal dose for a man of 65 kilos. would be about 585 grams; if administered by subcutaneous injection the dose would be less.

α-Naphthol is superior to β-naphthol by reason of its greater antiseptic properties and its feebler toxic action. C. H. B.

Poisoning by Carbonic Oxide. By N. GRÉHANT (*Compt. rend.*, **106**, 289).—The blood absorbs carbonic oxide from an atmosphere containing only 0·02 per cent. of the gas. If the atmosphere contains 0·1 per cent. of carbonic oxide, half the hæmoglobin in the blood will combine with this gas. 100 c.c. of the blood of a dog poisoned by an atmosphere containing 0·1 per cent. of carbonic oxide contained the following gases:—

	Normal.	Poisoned.
Carbonic anhydride....	47·0 c.c.	50·0 c.c.
Oxygen..............	27·0 „	14·2 „
Nitrogen.............	1·5 „	1·5 „

On treating the poisoned blood with acetic acid at 100°, it evolved 14·4 c.c. of carbonic oxide.

The analysis of the gases from the blood is of great value in supposed cases of fatal poisoning by carbonic oxide. C. H. B.

Toxic Action of Bases produced by Alcoholic Fermentation. By R. WURTZ (*Compt. rend.*, **106**, 363—364).—The base, $C_7H_{10}N_2$, isolated by Morin (this vol., p. 572) exerts a moderate toxic action, and produces general stupefaction and reduced sensibility, with frequent micturition and dilatation of the pupil, which becomes insensitive to light. These symptoms are followed by coma and death. When administered to a rabbit by subcutaneous injection, the fatal dose is 1 gram per kilo. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

New Lactic Acid Ferment occurring in Malt Wort. By P. LINDNER (*Chem. Centr.*, 1887, 1507, from *Centr. Bakteriol*, **2**, 340—342).—Cultivations of this sarcina formed organisms which behave similarly to pediococcus from beer. In neutral malt extract, it produces a sediment and cloudiness as well as a strong acid reaction after cultivation for 24 hours at 41°. The acid is lactic. It also changes the colour of the nutrient solution. The organism does not grow actively on potato, only a thin, microscopical film being formed. It grows very well on gelatin in the absence of air.

Although most of the sarcina isolated from beer have the power of forming lactic acid, none possess it to such a degree as this organism isolated from malt wort. The author provisionally calls it *Pediococcus acidi lactici*. J. P. L.

Influence of Certain Rays of the Solar Spectrum on Root Absorption and on the Growth of Plants. By A. B. GRIFFITHS and MRS. GRIFFITHS (*Proc. Roy. Soc. Edin.*, **123**, 125—129).—Mustard and bean plants grown in calcareous soil, to which had been added a definite amount of ferrous sulphate, were exposed daily to various portions of the solar spectrum. Incineration of the plants showed that the greatest amount of ferric oxide was contained in those exposed to the yellow-green rays D—E, under the influence of which rays also the greatest amount of oxygen is evolved. Examination of the plant for sulphur as representing the albuminoïds, which must have derived their sulphur from the ferrous sulphate, showed that the maximum of albuminoïds was attained under the influence of the rays D—E. E. W. P.

Plants Free from Chlorophyll acting like Chlorophyll-containing Plants. By F. HÜPPE (*Chem. Centr.*, 1887, 1512, from *Ntf. Vers. zu Wiesbaden*, **60**, 244—245).—From researches on the biology of bacteria, it appears that the qualitative differences which exist between bacteria and other plants can be referred, as regards their function, to some common origin. There is sufficient evidence to show that so far as the action of light is concerned, gradation exists between functionally undifferentiated protoplasm and ordinary chlorophyll.

The author corroborates Heraeus's statement that a nitrifying organism exists which can synthesise carbohydrates from carbonic anhydride.

The assimilation of carbonic anhydride does not therefore appear to be dependent necessarily on a specially differentiated part of protoplasm like chlorophyll. J. P. L.

Respiration of Yeast Cells at Different Temperatures. By GRÉHANT and QUINQUAUD (*Compt. rend.*, **106**, 609—610).—The amount of carbonic anhydride evolved and of oxygen absorbed by yeast cells in pure water in contact with a known volume of air was determined at different temperatures. The total amount of carbonic anhydride produced and of oxygen absorbed increases with rise of temperature from 0° to 46·3°, and the ratio of carbonic anhydride to oxygen also increases. It follows that the respiration of yeast is not analogous to that of mushrooms or of plants containing chlorophyll, since, according to Bonnier and Mangin, the ratio of carbonic anhydride to oxygen does not vary with the temperature in these cases.

C. H. B.

Presence of Saccharose in Unripe Potatoes. By E. SCHULZE and T. SELIWANOFF (*Landw. Versuchs-Stat.*, 1887, 403—407).—When the unripe tubers are dried and extracted with 90 per cent. alcohol, an extract is obtained which yields a saccharate with strontium hydroxide. The saccharose from this saccharate the authors show is identical with ordinary cane-sugar. H. Müller (*Landw. Jahrbuch.*, 1882, 774) considered that saccharose was an intermediate product between starch and glucose, and it is contended that the research now published supports this theory. E. W. P.

Detection of Saccharose in Vegetable Substances. By E. SCHULZE (*Landw. Versuchs-Stat.*, 1887, 408—413).—Employing the strontium process, the author has obtained saccharose from the etiolated shoots of potato tubers, as also from the pollen of *Pinus sylvestris*, carrots, and the leaves of the grape vines. It appears that the strontium precipitate in addition to saccharose contains mellitose and β-galactan; mellitose and saccharose are readily distinguishable by their crystals, as also by the formation of invertin by the one, and the production of mucic acid by oxidation of mellitose. To obtain saccharose in a crystalline form, when mixed with mellitose and galactose, it is recommended to evaporate the solution to a syrup, and then extract with hot alcohol, and after filtration to allow crystallisation to take place slowly. E. W. P.

Composition of Etiolated Potato Sprouts. By T. SELIWANOFF (*Landw. Versuchs-Stat.*, 1887, 414—417). — In the dry etiolated sprouts were found 3·45 per cent. of saccharose as well as asparagine and glucose; the amount of asparagine was 2·95 per cent. on the dry substance, and the albuminoïds amounted to 18·56 per cent. E. W. P.

Action of Ether on Plant-life. By G. BRENSTEIN (*Arch. Pharm.* [3], **25**, 918—924).—An atmosphere saturated with ether kills barley and wheat sprouts within 30 minutes. Five minutes' exposure affected the plants, the tips of the leaves, consequently the oldest portions, being first killed; whilst the basal portions of the leaves, and therefore the youngest parts, resisted longest. Experiments made with portions of the plant *Elodea canadensis* showed that five minutes' exposure to the ether atmosphere sufficed to kill the plant; the bicellular leaf texture of this plant seems to be more permeable to ether than are the leaves of wheat and barley. J. T.

Aluminium as a Natural Constituent of Wheat Flour. By W. C. YOUNG (*Analyst*, **13**, 5—6).—The author confirms the statement of Yoshida (Trans., 1887, 748) as to the occurrence of a minute quantity of aluminium in wheat, and shows that practically the whole of it is associated with the gluten. A sample of the best Vienna flour gave 0·0075 per cent. of aluminium phosphate. The gluten from 250 grams of this flour was dissolved in acetic acid to purify it, and the solution yielded aluminium phosphate amounting to 0·0074 per 100 of flour. M. J. S.

General Conditions favourable to the Absorption of Atmospheric Nitrogen by Vegetable Soils. By BERTHELOT (*Compt. rend.*, **106**, 569—574).—The author has previously shown that soil absorbs nitrogen directly from the atmosphere, the absorption taking place under the influence of minute organisms. Oxygen must be present as well as nitrogen, since in absence of the former the anærobic organisms increase, and a low form of green vegetation grows on the surface of the soil. These either actually destroy the aërobic organisms to which the absorption of nitrogen is due, or they remove the oxygen which is essential to their existence. The anaërobic organisms indeed actually cause a certain loss of nitrogen, probably by reduction. The porosity of the soil is essential in the highest degree, and it should contain not less than 2 per cent. and not more than 15 per cent. of water. With a higher proportion, the soil loses its porosity, especially if it is continually wet without alternating periods of dryness. Nitrification will not take place in dry soils, hence it follows that the two processes are not analogous. The temperature should not be below 10° nor above 50°. A soil which is not bearing a crop loses its power of absorbing any further quantity of nitrogen after a certain time. C. H. B.

Natural and Artificial Manures. By W. I. MACADAM (*J. Soc. Chem. Ind.*, 7, 79—100).—A complete review of manures, both natural and artificial, with numerous analyses, giving the composition of the different manures. D. B.

Analytical Chemistry.

Simplified Chromometer for Comparison of Moderately Deep Tints. By C. H. RIDSDALE (*J. Soc. Chem. Ind.*, 7, 70—73).—Three graduated glass comparison tubes are suspended as near each other as possible through a perforated strip of wood, supported at each end by a thick glass rod, terminating at the lower extremity in the base board. The centre tube containing the standard is sealed at the bottom, whilst the two side-tubes each have a $\frac{3}{16}$ hole in them. In all three is a small enamel glass cylinder, the top of which is the zero line, and the graduation continues upwards. A grip arrangement holding three test-tubes is clamped on the two glass supports. These slide easily over the comparison tubes, the tops when in their lowest position reaching to the zero mark of the graduated tubes. The process of comparison is as follows:—Fill the centre tube up to a certain mark with solution of standard depth of tint, pour the solution to be compared into one of the side-tubes, when it will immediately run into the test-tube beneath; when this is nearly full, look right down the two comparison tubes and raise the test-tube containing the solution to be compared, until the depth of tint is equal to that of the standard. Then read off the number of divisions required and calculate:—

$$\frac{\text{Number div. stan.} \times \text{per cent. stan.}}{\text{Number div. sol. to be tested}} = \text{per cent. sought.}$$

The author has used this apparatus chiefly for testing carbon in steel by the Eggertz colour method. D. B.

Behaviour of Congo-red towards some Acids and Salts. By E. BRÜCKE (*Monatsh.*, 9, 31—41; compare Abstr., 1887, 986;

this vol., p. 381).—It was previously shown that carbonic anhydride colours Congo-red purple-violet; boric acid also colours it violet; with salicylic acid, a blue or slightly violet colour is obtained. Arsenious acid seems to have no action on it. The blue colour obtained by the action of acids on Congo-red is insoluble in water, and can be separated by filtration. When an aqueous Congo-red solution is treated with sufficient acid to produce a violet colour and then heated at 50° to 60°, the solution becomes purple and then red; on cooling, the original violet colour returns. This change of colour does not take place in presence of an excess of acid, except in the case of boric acid.

When so much acid is added to a solution of Congo-red that the latter becomes just blue, the addition of an acid tartrate or acetate produces a violet or red colour; more or less acid must be added to bring back the blue colour, according to the amount and nature of the salt. Congo-red is therefore unsuitable as an indicator in organic and inorganic analysis.

Congo-red can be used to show the presence of small amounts of acids in fats; an aqueous solution shaken with rancid oil becomes at once bluish-violet. When butyric acid is added to Congo-red dissolved in water, the latter becomes blue from the butyric acid dissolved; on boiling, the butyric acid takes up all the colour, leaving the aqueous solution colourless. An alcoholic solution of Congo-red is not changed by butyric or oleic acids.

Glycerol, even when containing sufficient hydrochloric acid to slightly redden litmus, will bring back the red colour of Congo-red previously made blue with a little hydrochloric acid.

The changes of colour produced by several salts are also described.

N. H. M.

Volumetric Estimation of Iodine in the Presence of Chlorine and Bromine. By N. McCulloch (*Chem. News*, **57**, 135—136).—By the following method, iodine may be estimated in the presence of bromine and chlorine without previous removal of the latter elements (compare this vol., p. 526). The solution containing the chloride, bromide, and iodide is mixed with its own bulk of strong hydrochloric acid, and 20 to 30 fluid grains of chloroform; standardised permanganate is dropped in, with agitation, until the iodidne colour at first produced in the chloroform is again discharged owing to the formation of colourless iodine monochloride. Iodine bromide in strong solution colours the chloroform faint yellowish-pink, which cannot however be mistaken for the iodine coloration. The process cannot be employed in the presence of free hydrogen bromide and cyanide; the presence of the latter causes high results.

D. A. L.

Detection of Iodine in Urine. By C. Schwarz (*Arch. Pharm.* [3], **25**, 1061, from *Pharm. Zeit.*, **32**, 631).—The following method succeeds perfectly without previous concentration of the urine:—10 c.c. of urine is mixed with 2 c.c. of dilute sulphuric acid (1 : 5), with 5 drops of a 1 per cent. starch solution freshly prepared, and the whole well shaken; to the mixture is now added, drop by drop, a 1 per cent. potassium nitrite solution, when the characteristic violet or blue iodine colour appears immediately, and as quickly disappears on adding a drop or two of decinormal sodium thiosulphate solution. More delicate still is the carbon bisulphide test when made under similar conditions; the urine to which a little bisulphide has been added must be vigorously shaken after the addition of each single drop of nitrite. Numerous urines examined have invariably given positive results whether the iodine has been applied internally or externally, and whatever compound has been employed. J. T.

Estimation of Active Oxygen by means of Tetramethylparaphenylenediamine. By C. Wurster (*Ber.*, **21**, 921—924).—The property of tetramethylparaphenylenediamine to yield a blue colour when oxidised with one atomic proportion of oxygen, and to form a colourless compound when further oxidised with six atomic proportions, can be employed as a means of estimating approximately the oxidising power of plant fluids, saliva, &c. Test-papers are used, and the colour produced by the action of one or two drops of the liquid on one of these is compared with a colour scale consisting of eight shades of colour, whose values in terms of "active" oxygen are estimated from the titre of the iodine solutions which produce similar colours on the "tetra-paper." The oxidising power of air can be estimated in like manner, by drawing a known volume of air through a tube closed at one end with a piece of "tetra-paper" moistened with dilute glycerol. W. P. W.

Determination of Sulphur in Oils. By A. H. Allen (*Analyst*, **13**, 43—45).—The oil, a blast-furnace creosote oil containing 0·088 per cent. of sulphur, was mixed with purified methylated spirit (5 grams of oil to 45 of spirit), and the mixture after saturation with solid ammonium carbonate was burnt in a lamp, fitted by a bung into the wider end of a curved adapter. The small end of the adapter was connected with a tube bent downwards at a right angle, and passing nearly to the bottom of a wider tube (the glass jacket of a Liebig's condenser) filled with wetted glass balls. The lower end of this was furnished with a glass stopcock for drawing off the condensed liquid. The upper tubulus was connected with an aspirator. For working on rape oil, an equal weight of "kerosine" was used as diluent, and the ammonium carbonate was in this case suspended above the flame in a porcelain crucible. A sample of rape oil was found to contain 0·017 per cent. of sulphur. The ammonium sulphite in the condensed liquid was oxidised with bromine before precipitating with barium chloride. M. J. S.

Ferric Ferricyanide as a Reagent for Detecting Traces of Reducing Gases. By Crum Brown (*Proc. Roy. Soc. Edin.*, **124**, 419).—The brown solution obtained when ferric chloride and potassium ferricyanide are mixed, and which contains ferric ferricyanide, is absorbed by strips of filter paper; these test-papers become blue in the presence of reducing gases, such as sulphurous anhydride, hydrogen sulphide, &c. As nitrous fumes also blue the test-papers, traces of them can be detected by the additional use of iodised starch-paper. E. W. P.

Kjeldahl's Method of Estimating Nitrogen. By R. MELDOLA and E. R. MORITZ (*J. Soc. Chem. Ind.*, 7, 63).—As this process, especially when applied to the determination of minute quantities of nitrogen, requires the use of pure sulphuric acid, the authors recommend a method by which the acid may be freed from nitrogenous impurity. This is based on the well-known decomposition of ammonia by nitrous acid, the authors being of opinion that the traces of nitrogen found in impure sulphuric acid represent small quantities of ammonium sulphate. About 0·05 gram of potassium nitrite is added to 10 c.c. of sulphuric acid, and the mixture heated to expel the excess of nitrous acid. D. B.

Determination of Vanadium in the Presence of Chromium, Aluminium, and Phosphorus. By C. H. RIDSDALE (*J. Soc. Chem. Ind.*, 7, 73—77).—After thoroughly examining all the best methods of estimating vanadium, the author found Lindemann's process (*Chem. News*, 1883, January 5) to be the most rapid and trustworthy. He has applied this method, in conjunction with a process devised by him for the estimation of other substances, to the analysis of vanadium in slag. The mode of procedure is described in detail in the original paper. D. B.

Estimation of Reduced Phosphates. By V. DIRCKS and F. WERENSKIOLD (*Landw. Versuchs-Stat.*, 1887, 425—453).—The authors have put to the proof the various processes employed for the estimation and separation of tricalcium from mono- and di-calcium phosphates, namely, the various modifications of the ammonium citrate methods. They find that although none of the methods give a really satisfactory and exact result, Petermann's process is perhaps the most trustworthy. E. W. P.

Volumetric Estimation of Boric Acid. By H. WILL (*Arch. Pharm.* [3], 25, 1101—1113.)—A rapid and fairly accurate estimation of free boric acid can be made by titration with a standard baryta solution, which is added to the solution of the acid until the turbidity appearing at first is completely and exactly removed. The amount of barium hydroxide used is exactly double the equivalent of the boric acid present, according to the equation $4H_3BO_3 + Ba(HO)_2 = BaB_4O_7 + 7H_2O$. Schwarz has recently shown in the *Pharm. Zeit.* that the boric acid set free from borax by nitric acid does not affect Congo-red, whilst the slightest excess of nitric acid produces a blue-violet tint, and on this has based an obvious method for estimating the amount of acid in the borax. The boric acid thus set free can also be determined by titration with baryta-water as above, or ethyl or methyl-orange may be substituted for the Congo-red, and hydrochloric acid may be used to decompose the borax. A mixture of free boric acid and borax solution can be dealt with by a combination of the two methods, that is, by first titrating with standard acid, and then titrating the total boric acid with baryta-water. Instead of first setting free the acid, a solution of pure borax can be titrated directly by baryta solution, but only half the amount of standard solution is now required, since the equivalent amount of sodium hydroxide set free replaces the other half of baryta.

In the presence of borax, chlorides can be estimated directly by means of silver nitrate, using potassium chromate as indicator; free boric acid interferes with the reaction in this case; the free acid is first determined by means of baryta solution; then normal soda solution equivalent to at least half the baryta solution employed is added, and then dilute sulphuric acid until neutral; the chlorides can now be directly estimated. The addition of soda solution may be omitted when estimating chlorides in the presence of little free boric acid and much borax just as in the presence of borax only. Of course, the chlorides and boric acid can be determined in separate portions, and can be directly titrated in the former after neutralisation by means of soda solution.

Boric acid in presence of sulphates is estimated by the aid of phenacetolin as an indicator. To the solution of boric acid and sulphates, two drops of an alcoholic solution of the indicator are added, and then standard baryta solution until a faint yellow tint appears; normal hydrochloric acid is now added until a faint rose tint becomes decided rose colour, the corresponding amount of baryta solution is deducted from the original amount taken, and the remainder indicates the boric acid. A further addition of hydrochloric acid until the colour changes from rose to yellow with the last drop, serves as a control estimation; the acid thus taken being equivalent to the baryta combined with the boric acid. Halving the baryta and calculating the equivalent boric acid, this should agree with the amount first formed. Sulphates of the alkalis and of the alkaline earths, excepting magnesia, may be present. A little practice is required to get the rose colour accurately, and it is found better to use normal acid rather than a weaker one. For the estimation of borax in the presence of sulphates, Schwarz's method can be directly applied. J. T.

Separation of Barium, Strontium, and Calcium. By A. Russmann (*Chem. Centr.*, 1887, 1446—1447.—*Frerich's Method.*—By using the potassium chromate method for a barium salt alone, approximately correct results are obtained, but for mixtures in which barium and strontium are to be separated there should not be (1) more than 15 parts of strontium to 50 parts of barium, otherwise strontium will be precipitated as chromate; (2) nor more than 0·5 to 1 per cent. of barium and strontium in the solution. Calcium, if it is present, does not influence the precipitation of the barium. On ignition, some of the chromate is reduced to chromium oxide by the filter-paper.

Volumetric Estimation of Barium in Chromate of Barium.—None of the methods give exact results, because the hydrochloric acid used always decomposes some of the iodide of potassium even if the acid is only acting for a short time. The best results were obtained by dissolving the precipitated chromate in weak hydrochloric acid, adding the iodide of potassium, and immediately titrating after dilution. Better and quicker results are obtained by this method than by Crismer's method (*Ber.*, **17**, 642).

Diehl's Method (*J. pr. Chem.*, **79**, 430).—This method depends on the solubility of calcium sulphate in sodium thiosulphate. The barium sulphate carries down an important quantity of calcium sulphate which cannot be dissolved even by long-continued digestion with warm sodium thiosulphate. Barium sulphate is, however, quite insoluble in the sodium thiosulphate. Besides this objection, the sulphur which separates, and agglomerates when the estimation of the lime is proceeded with, encloses some lime, or, again, a part of the lime may be converted into sulphate.

Separation of Barium and Calcium with Sulphuric Acid (1 : 300).—This process gives good results both when there is much calcium and little barium, and when there is much barium (100 parts) and little calcium (1 part). Lime is never precipitated.

Sidersky's Method (Abstr., 1883, 509) (*Ammonium Sulphate and Oxalate*).—Sidersky's second method gives good results, namely, precipitation of strontium and calcium salts with ammonium sulphate and oxalate in a solution acidified with hydrochloric acid. Strontium sulphate only is precipitated if the acid used contains not less than 8·5 per cent. of HCl. Calcium and barium may also be satisfactorily separated by this process.

Bloxam's Method for Detecting Calcium in Presence of Strontium (*Calcium Ammonium Arsenate*, Abstr., 1886, 920).—The method is very useful as a qualitative test; 1 part of calcium in presence of 500 parts of strontium can be readily detected. For quantitative determinations the process is inexact.

Fleischer's Method.—The process is useful for solutions in which barium and calcium are present but no magnesium.

Leison's Method.—The volumetric estimation of oxalates of the alkaline earths by the use of potassium permanganate in acid solution gives good results. It is quicker, however, to ignite the precipitate.

J. P. L.

Separation of Copper and Arsenic, and their Estimation in a Case of Poisoning. By P. GUCCI (*Chem. Centr.*, 1887, 1528, from *Atti della Soc. Toscana di Sc. Naturali*, 5, 287—289).—If copper and arsenic, occurring together in intestinal contents, be precipitated as sulphides after treatment of the intestinal matter with potassium chlorate and hydrochloric acid, their separation by means of alkali sulphides is unsatisfactory. The copper sulphide is in such a fine state of division that it cannot be separated by filtration, and an important amount also remains in solution.

The author treats the washed and dried sulphides with fuming nitric acid, evaporates to dryness, and repeats the treatment. The final residue is then melted with soda and potassium nitrate. The melt is dissolved in water and nitric acid, the copper precipitated with potash, and weighed as oxide. From the filtrate, the arsenic is precipitated either as ammonio-magnesic arsenate or as arsenic sulphide.

J. P. L.

Detection of Mercury in Urine. By K. ALT (*Arch. Pharm.* [3], 25, 969—970, from *Centr. Med. Wiss.*).—The urine is acidified with hydrochloric acid, and in it is immersed a piece of tinsel (a zinc-copper alloy) about 8 × 4 cm., fastened to the cork of the vessel.

The liquid is heated at 60° for half an hour, and then allowed to remain for 15 hours, so that the free mercury collects on the upper surface of the tinsel. The latter is taken out, washed with water, dried with alcohol and ether, carefully folded, and placed in a test-tube, in which it is heated for half a minute, during which a trace of iodine is brought into the tube; the presence of mercury is immediately shown by the appearance of a film of iodide on the tube; 0·016 mgrm. of mercuric chloride can thus be detected in 100 c.c. of urine, whilst the limit of Fürbringer's test is 0·2 mgrm., and that of Müller's is 0·06 mgrm. J. T.

Estimation of Iron. By C. SCHACHT (*Arch. Pharm.* [3], **25**, 906—910).—In a well-stoppered flask, 1 gram of *ferrum oxydatum saccharat. solubile* is covered with 5 c.c. of hydrochloric of 1·12 sp. gr.; after standing 10 minutes, 50 c.c. of water and 0·5 gram of potassium iodide are added, and the flask is set in a warm place for an hour, when the free iodine is titrated by means of decinormal sodium thiosulphate solution. To estimate the iron in *ferrum carbonic. saccharat.*, 0·5 gram is heated with 5 c.c. of dilute sulphuric acid until completely dissolved. After cooling, permanganate solution is added to the clear solution just to faintly tint it, then 1 gram of potassium iodide as above. By this short method fairly concordant results were obtained with numerous pharmaceutical preparations of iron. J. T.

Aluminium in Wheat. By A. H. ALLEN (*Analyst*, **13**, 41—43).—From the statements of various food-analysts, it seems that aluminium in minute proportions is a normal constituent of wheat, the amount corresponding with about 8 grains of alum in the 4-lb. loaf. A method of determining the alumina present, otherwise than as silicate, consists in dissolving the starch by means of malt extract, fermenting the solution with yeast, acidifying with nitric acid, filtering, evaporating, and igniting the residue, then precipitating the alumina as phosphate in the usual way. M. J. S.

Separation of Iron, Nickel, Cobalt, Manganese, Zinc, and Aluminium. By T. MOORE (*Chem. News*, **57**, 125).—The present process is a modification of the one previously described (Abstr., 1887, 1141). Excess of solid sodium hydrogen carbonate is mixed with the cold, concentrated, and slightly acid solution, potassium cyanide is then added until the precipitate is dissolved, and the whole heated until the solution assumes the yellow colour of the ferrocyanide, and is perfectly clear; when, however, alumina is present, the solution remains somewhat turbid, but is clarified by a few drops of potash. To separate nickel from iron, this solution when cool is mixed with a large excess of moderately strong potassium hydroxide, and treated with chlorine until the nickel hydroxide is completely converted into the peroxide, which is separated and treated in the usual manner for electrolytic deposition.

Alumina may be separated from iron, nickel, and cobalt by boiling the clear solution of the mixed ferrocyanides with ammonium chloride. To separate manganese from iron, nickel, and cobalt, the above clear solution is best precipitated by means of hydrogen sulphide, the manganese is rapidly and completely precipitated as sulphide, and is easily washed, &c. When, however, the clear solution is boiled with ammonium sulphide until ammonia ceases to be evolved, zinc sulphide alone is precipitated, and, therefore, this forms a ready method of separating zinc from iron, nickel, and cobalt. D. A. L.

Separating Tin from Antimony and Estimation of these Metals in Siliceous Slags and Alloys. By H. N. Warren (*Chem. News*, **57**, 124—125).—The powdered slag is dissolved in a mixture of equal parts of hydrochloric and hydrofluoric acids, the solution filtered, heated, saturated with hydrogen sulphide, and the precipitate boiled with sodium hydroxide. The sulphides of tin and antimony are then reprecipitated by means of hydrochloric acid, and decomposed with aqua regia; the solution is evaporated to a small bulk, diluted with weak hydrochloric acid, and treated with potassium ferrocyanide, until it assumes a clear, blue colour, when the solution is allowed to boil. The tin is precipitated as stannic ferrocyanide, whilst the antimony remains in solution. Both metals are then easily determined. Alloys are dissolved in aqua regia instead of the mixture of hydrogen fluoride and chloride. D. A. L.

Chloroform Testing. By G. Vulpius (*Arch. Pharm.* [3], **25**, 998—1001).—Chloroform for medicinal use should be required to pass the following test:—10 c.c. mixed with 2 c.c. of water, 2 drops of phenolphthaleïn solution, and 1 drop of decinormal potash solution, is shaken repeatedly in a stoppered flask which it nearly fills; the red colour should not disappear in 24 hours; and the usual test with sulphuric acid should not give a perceptible yellow colour within one day. J. T.

Estimation of Chloroform, and its Solubility in Water. By G. Chancel and F. Parmentier (*Compt. rend.*, **106**, 577).—The method for the estimation of chloroform described by St. Martin (this vol., p. 570), has previously been described by the authors (Abstr., 1885, 363). They find that the solubility in water decreases from 0° to 54·9°, the amount dissolved per litre varying from 9·87 to 7·75 grams. They did not obtain any saturated solution containing only 6·4 grams as stated by St. Martin. C. H. B.

Estimation of Starch. By J. N. Spence (*J. Soc. Chem. Ind.*, **7**, 77).—Having occasion to estimate the amount of starch in pepper, the author tried Asboth's process (Abstr., 1887, 868), but could not obtain constant results. Asboth recommends the addition of the baryta-water in the cold, but the author finds that by adding it to the hot solution, a better marked compound is obtained. The author also shows that the barium-compound is soluble in water, but is precipitated again by the alcohol, it is therefore not insoluble as stated. The standard baryta-water should never be below the strength capable of saturating 90 c.c. of decinormal hydrochloric acid, otherwise it is possible to form more than one compound, the nature of each depending on the strength of the baryta-water. D. B.

Detection of Acetic Acid in Presence of Morphine. By G. S. JOHNSON (*Chem. News*, **57**, 83).—An aqueous solution of morphine acetate is treated with a solution of ferric chloride, avoiding excess of acid; the morphine blue colour develops at once, but on warming gives way to the blood-red colour of ferric acetate. 1 part of morphine acetate in 870 parts of water may be detected by this means. D. A. L.

Action of Sulphur Chloride on Oils. By T. T. P. B. WARREN (*Chem. News*, **57**, 113; compare this vol., p. 199).—While examining oils or oily mixtures, the melting point, consistency, viscosity, and other properties should be noted at the various stages:—5 grams of the oil are mixed first with 2 c.c. of carbon bisulphide, then with 2 c.c. of a mixture of equal parts of carbon bisulphide and sulphur chloride, and heated; at the completion of the reaction, the volatile products are expelled, and the appearance of the mass noted. This is then transferred to the filter-tube, washed with carbon bisulphide, and the extracted matter weighed. The colour, odour, &c., of both the insoluble and soluble products will in many cases indicate what oils they are. If the extract is turbid from deposited sulphur, the oil-mass, after it has been weighed, is treated with ether saturated with sulphur, and the weight of any residual sulphur is then deducted from the weight of the oil. The author gives an example of his mode of dealing with a mixture of two oils, both yielding solid products with sulphur chloride (*loc. cit.*), and points out difficulties arising from the solvent action of one oil on another. He has found arachis oil largely adulterated with cotton-seed oil. D. A. L.

Detection of Cotton-seed Oil. By E. MILLIAU (*Compt. rend.*, **106**, 550—551).—If the purified fatty acids obtained from cotton-seed oil are dissolved in 3 vols. of alcohol of 90°, and boiled for some minutes with 2 c.c. of a 3 per cent. solution of silver nitrate, the latter is reduced, and the silver rises to the surface of the liquid in the form of a pasty mass. This reaction is not obtained with the fatty acids from olive oil, and is sufficiently delicate to detect 1 per cent. of cotton-seed oil in olive oil.

When the dried fatty acids from oil of sesame are mixed with an equal volume of hydrochloric acid containing sugar, a blood-red coloration is immediately produced. The fatty acids of olive oil and other oils do not give this reaction, and it will detect 1 per cent. of oil of sesame in a mixture of oils. If the test is made directly on the oils, the result is uncertain, since the aqueous liquid which runs from the olives in the process of pressing gives a similar coloration. By operating on the separated fatty acids, however, the uncertainty is removed. C. H. B.

Estimation of Fat in Fodder. By L. BÜHRING (*Landw. Versuchs-Stat.*, 1887, 419—423).—It is advisable for the correct estimation of fat in fodders of all kinds, that the sample should be thoroughly dried, either in a vacuum or at 100°, also that the ether should contain no water; as otherwise, carbohydrates are dissolved, which materially raise the percentage of fat. Several analyses are given to show the effect of drying. E. W. P.

Relation between Specific Gravity, Fat, and Solids in Milk. By P. Vieth (*Analyst*, 49—51).—Hehner and Fleischmann have published formulæ (for the latter see this vol., p. 94) by which the fat in milk can be calculated from the specific gravity and amount of total solids. With Hehner's formula, the difference between the calculated percentage of fat and that determined by extraction from a paper coil (Adams' process) is small with low percentages of fat, but considerable when the percentage of fat is large. Comparing Fleischmann's formula with the results of extraction after drying on gypsum, the differences never exceed 0·2 per cent. (above or below), and the average difference in 530 analyses was 0·02 per cent. These formulæ are only applicable where, as in cow's milk, the ash, proteïds, and sugar are in the ratio 1 : 5 : 6. In human milk the ratio is 1 : 5 : 10, and in mare's milk, 1 : 6 : 23. M. J. S.

Action of Alcohol on Butter Fat. By C. B. Cochran (*Analyst*, **13**, 55—57).—To test artificial butter for added tributyrates, it has been recommended to treat the sample with alcohol, and ascertain by Reichert's process whether the amount of volatile acid in the undissolved residue is less than in the original substance. Genuine butter gives, however, precisely this result. Several samples of genuine butter were treated with alcohol at 23—25°, using 10 c.c. of 90 per cent. alcohol to 1 gram. The percentage of volatile fatty acid in the undissolved residue was in every case reduced, but in no case did the distillate from 2·5 grams of the undissolved portion require less than 9 c.c. of N/10 alkali. This number is therefore accepted as the minimum for a genuine butter, after treatment with the above proportion of alcohol, and it is suggested that adulteration is more likely to be detected by applying Reichert's method to the undissolved fat than by using it on the original butter.

It is noticed that genuine butter which has been kept for some time may in Reichert's process give results falling below the standard of 12·5 c.c. of N/10 alkali for 2·5 grams of butter. In one case of a butter 10 months old, but in good preservation and palatable, only 10·5 c.c. were required. M. J. S.

Bases in Alcoholic Liquids. By L. Lindet (*Compt. rend.*, **106**, 280—283).—500—1000 c.c. of the liquid at 50° Gay-Lussac is mixed with 20 grams of strong sulphuric acid, well agitated and distilled until all alcohol and water is expelled. 0·5 gram of mercury is added, and the operation conducted exactly as in the estimation of nitrogen by Kjeldahl's process, the nitrogen of the bases being obtained in the form of ammonia. One part of base in 1,000,000 parts of alcohol can be detected, and the distillate contains no bases.

The examination of several alcoholic liquids in this way shows that the amount of ammonia per litre of liquid varies from 0·40 to

23·05 mgrms. Alcohols obtained by the fermentation of grain contain the smallest amount; the quantity in rum is much higher than in other spirits, whilst the alcohol from beetroot molasses contains a very much higher proportion than any of the others. C. H. B.

Estimation of Morphine in Opium. By A. KREMEL (*Chem. Centr.*, 1887, 1529—1530, from *Pharm. Post*, **20**, 661).—5 grams of opium powder is digested with 75 c.c. of lime water for 12 hours with frequent shaking; 60 c.c. of the filtered liquid, which should not have an alkaline reaction, is mixed with 15 c.c. of ether and 4 c.c. of normal ammonia in a weighed flask. The flask is corked and the contents mixed with gentle shaking. The ether is decanted after remaining at 10—15° for 6 to 8 hours, another 5 c.c. of ether is added, and this again decanted after gentle shaking. The crystals of morphine separated with the ether are collected on a small filter. These crystals, with those remaining in the flask, are washed with 5 c.c. of water, and both finally dried at 100° and weighed.

J. P. L.

Estimation of Morphine in Opium. By E. F. TESCHEMACHER and J. D. SMITH (*Chem. News*, **57**, 93—95, 103—105).—The authors review and criticise the methods recommended for the determination of the morphine in opium, and point out that those depending on the use of lime, much alcohol, or much water, are untrustworthy; in this category they include the Squibb-Flückiger method even as modified by Stillwell (Abstr., 1887, 403), the Hager-Jacobsen, Merck's, the British Pharmacopœia, and other methods. It is noteworthy that any one of these methods will give concordant results when applied in the same manner to the same sample of opium, but nevertheless the results are erroneous. A small quantity of alcohol is necessary, as otherwise the morphine is precipitated in a form difficult to wash, but the quantity should not exceed 50 grains of alcohol to 200 grains of opium; the authors approve the idea suggested by Allen, of finally titrating the morphine, as this excludes errors due to adherent colouring matter, &c. Their own method is fully described, and is briefly as follows:—Exhaust 200 grains of opium with warm distilled water, concentrate steadily to a thin syrup, mix with 50 fluid grains of alcohol, sp. gr. about 0·820, and about 600 fluid grains of ether, then add 50 fluid grains of ammonia, sp. gr. 0·935, shake well, and agitate occasionally during the next 18 hours, filter, and to remove colouring matter, &c., wash first with 80 per cent. spirit saturated with morphine, then with morphinated water. Dry carefully, pulverise, digest with benzene, filter, dry, weigh, and finally titrate with standard hydrochloric acid, using litmus as indicator, &c. Benzene dissolves all other opium alkaloïds except morphine and narceïne, and the latter is removed in the earlier stages of this process. D. A. L.

Estimation of Morphine in Opium. By R. WILLIAMS (*Chem. News*, **57**, 134—135).—The author's experience with the processes generally employed for the estimation of morphine in opium confirms the opinion expressed by Teschemacher and Smith (preceding

Abstract). The method he now employs is similar to that described by the latter authors, except that he prefers to extract the opium with cold instead of warm water, and uses 100 instead of 50 grains of alcohol. D. A. L.

Testing Neutral Quinine Salts. By L. SCHÄFER (*Arch. Pharm.* [3], **25**, 1041).—The oxalate test may be applied directly to those neutral quinine salts whose solubility in water is not less than that of quinine sulphate, for instance the hydrochloride, bromate, valerate. Thus a molecular quantity corresponding with 1 gram of the sulph. cryst. is weighed off and treated as described in the following Abstract. Collateral alkaloïd mixtures are indicated as sharply as in the case of the sulphates, except that, as with quinine valerate, a portion of the acid is lost during heating and it becomes alkaline, when a little more passes the test. J. T.

Estimation of Cinchonidine in Quinine Sulphate. By L. SCHÄFER (*Arch. Pharm.* [3], **25**, 1033—1041).—The ammonia method given by Kerner and Weller (Abstr., 1887, 1146) is shown to be quite fallacious, mainly owing to the readiness with which a double salt of quinine and cinchonidine sulphate is formed. Further, animal as well as vegetable fibres absorb variable quantities of the quinine alkaloïds, and the use of different kinds of filter-paper may produce a difference of 1 c.c. in the amount of ammonia solution used. Glass-wool filters should be employed. The oxalate test (Abstr., 1887, 623) is slightly modified on this account. 1 gram of quinine sulph. cryst. (0·85 gram completely dried sulphate) is boiled with 35 c.c. water in a small tared flask. To this is added 0·3 gram of neutral crystallised potassium carbonate (oxalate?) in 5 c.c. water, and the solution is made up to 41·3 c.c. The flask is kept at 20° and shaken occasionally during half an hour, when its contents are filtered through glass-wool, and to 10 c.c. a drop of officinal aqueous soda is added. No turbidity appears for some minutes if the original sulphate is pure. 1 per cent. of cinchonidine may thus be missed. 1½ per cent., however, gives an immediate turbidity, and larger quantities afford a precipitate. On filtering through glass-wool after one hour, 2 per cent. or more affords an immediate turbidity or a precipitate. J. T.

Colchicine-like Decomposition Product. By G. BAUMERT (*Arch. Pharm.* [3], **25**, 911—918).—In a supposed poisoning case, the Stas-Otto method was followed, and a substance closely resembling colchicine was found, although death had occurred twenty-two months previously. Parallel reactions made with pure colchicine differed in many cases from those obtained with the extract from the body; but when an aqueous extract was exhausted as far as possible by means of chloroform, and to this was added pure colchicine, the reactions then became identical with those given by the substance obtained from the body. Brieger, however, found that the substance was a peptone and physiologically inactive. Millon's reaction confirmed this. The peptone is also distinguishable from colchicine by giving a precipitate with picric acid, and with platinum chloride. J. T.

General and Physical Chemistry.

Spectrum of the Oxyhydrogen Flame. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **43**, 347—348).—The authors examined the third portion of the water spectrum extending into the ultra-violet. The lines fall into rhythmical groups, in which in many cases the distances between the lines measured in wave-lengths are in arithmetical progression. They find a striking resemblance between these groups and the groups A, B, and α, but no exact correspondence, as stated by Deslandres. They have found many of the lines predicted by Grünwald (Abstr., 1887, 1070). H. K. T.

Wave-lengths of two Red Lines in the Spectrum of Potassium. By H. DESLANDRES (*Compt. rend.*, **106**, 739).—By means of the electric arc and a Rutherfurd grating on glass, the author has determined the wave-lengths of the two potassium lines in the extreme red, and obtains for the stronger of the two the value 7663·0, and for the weaker 7696·3, D being taken as 5888·9. The mean value is 7679·65. Mascart by the same method found 7680·0, D being taken as 5888·0. C. H. B.

Ultra-violet Band-spectrum of Carbon Compounds. By H. DESLANDRES (*Compt. rend.*, **106**, 842—846).—The violet portion of the visible spectrum of carbon compounds in tubes under low pressure contains two groups of bands, the first of which is usually attributed to hydrocarbons, and is seen in the spectra of comets, whilst the second is most distinct under very low pressures, and was attributed by Ampère to carbonic oxide.

Carbonic oxide with a non-condensed spark under atmospheric pressure shows the first group only, whilst in the ultra-violet there is a faint trace of the carbon line $\lambda 2478·5$. Under very low pressures, however, this gas gives a very fine band spectrum in the ultra-violet, whilst in the visible spectrum group 1 is replaced by group 2, which is very brilliant. The ultra-violet spectrum includes, besides some bands of group 1, at least two distinct groups of bands, different in character from the visible bands, and readily distinguishable from one another. The bands in the 3rd group shade off on the more refrangible side, whilst those of the 4th group shade off in the opposite direction. Almost exactly the same spectra were obtained at low pressures with carbonic anhydride, acetylene, and cyanogen, although in the latter case the special bands of nitrogen and of cyanogen were recognisable. The exact origin of the bands was not determined. Their appearance is independent of the presence of nitrogen, and it seems probable that group 3 is due to some oxygen compound, whilst group 4 is due to the vapour of carbon only. The bands on the one hand and the lines on the other may be divided into series which, when represented on a scale of vibration-frequency, are in arithmetical progression, and are represented by the expression $Am^2 + a$, m being a whole number.

Group 3 has the same general appearance as group 2, usually attributed to carbonic oxide. The arrangement of the bands is simple, but the bands themselves are of complex structure.

Group 4 is different in appearance from any other carbon groups or nitrogen groups. It resembles the absorption-spectrum of iodine, and can be divided into five similar series, which are also in arithmetical progression. The bands are of comparatively simple structure, and are resolved into lines by two prisms of Iceland spar. Each band consists of two equal arithmetical series which are superposed on each other.

The division of the bands into series requires three successive operations, and the whole of the rays may be represented by a function of three parameters, m^2, n^2, p^2, of the form—

$$f(n^2, p^2) \times m^2 + Bn^2 + \phi(p^2),$$

m, n, and p being whole numbers. The law of periods in the more general vibratory motion of a solid, and in all similar problems of periodic vibrations, can likewise be represented as a function of three parameters, m^2, n^2, and p^2, which correspond with the three dimensions of space. The functions f and ϕ have not been accurately determined, but they seem to be of simple character, such as squares, inverse squares, or square roots. C. H. B.

Spectra of Meteorites. By J. N. Lockyer (*Proc. Roy. Soc.*, **43**, 117—156).—Observations were made on the spectra of elements and meteorites at low temperatures, namely, those of the bunsen flame, oxyhydrogen blowpipe, and vacuum discharge. The spectra were compared with those of the heavenly bodies. The following deductions are made:—The luminous phenomena of all heavenly bodies shining by their own light, with the exception of stars like the sun and Sirius, are produced by meteorites; the temperature of the meteorites in some cases is about that of the oxyhydrogen flame; the intensity of the light depends on the number of meteorites in the swarm; the main factor in the spectra produced is the ratio between the meteorites and the spaces between them; when the space is great the tenuity of the gases given off by the collisions is too great to give a luminous spectrum, later bright lines or flutings are produced, finally when the meteorites themselves are more crowded, and at a higher temperature, a continuous spectrum with dark lines will result; new stars are produced by the collision of swarms of meteorites, the lines being those of elements which give bright lines at low temperatures; the hydrogen spectrum in nebulæ is due to electrical excitation, the glow of a meteorite in a vacuum giving the hydrogen or carbon spectrum according to the amount of heat applied; the production of iron meteorites with embedded stones is due to the welding of the fused iron when meteorites collide. The author represents the consecutive conditions of stars by a curve, commencing with a low temperature swarm of meteorites, which by their gravitation produce a rise of temperature up to a certain height to afterwards decrease in temperature by radiation as the incandescent mass assumes first a vaporous and finally a solid condition. In the ascending branch are (1) nebulæ (bright lines); (2) stars with bright lines; (3) stars with little absorption, bright hydrogen lines; (4) stars with bright carbon, manganese, and zinc flutings; (5) stars with line absorption; at the top of the curve are stars with hydrogen absorption. In the descending branch are (1) stars with line absorption; (2) stars with carbon absorption. The sun is situated in the descending branch, as shown by the great thickening of the potassium line due to a concentration of the sun's atmosphere by condensation. H. K. T.

Galvanic Elements. By ROBERTS (*Dingl. polyt. J.*, **267**, 141).—The "permanganate element" is said to be free from chemical action when the circuit is broken. The solution consists of potassium permanganate, potassium dichromate, common salt, and sal-ammoniac. The negative electrode is a rod of zinc, the positive a carbon prism. The mean E.M.F. is 1·8 volts, the internal resistance 0·5 ohm. One element is sufficient to work an electric bell.

The "lead dioxide element" is prepared by mixing red lead with powdered potassium permanganate and sulphuric or hydrochloric acid. The mixture is poured into a mould containing carbon, and on solidifying forms a good porous conductor, which adheres firmly to the carbon, and has the same hardness. The electrode thus obtained is employed as a substitute for carbon with zinc and sulphuric acid, and yields a very constant current. By the application of a solution of salt and sodium dichromate still better results are obtained.

The electrolyte in the so-called "dry element" forms a thick, pasty substance prepared by mixing two saline compounds, each dissolved separately. D. B.

Experiments with Lippmann's Capillary Electrometer. By J. H. PRATT (*Amer. J. Sci.*, **35**, 143—151).—A description of the instrument used, which is of very simple construction, is given. The results show that it may be employed for measuring low potentials, up to 0·6 or 0·7 Daniell, and therefore for comparing the E.M.F. of different batteries, if only a known fraction of the current be used. Oxygen polarisation must be avoided, and only hydrogen polarisation employed. Under these conditions, the deflection of the meniscus may be taken as proportional to the E.M.F. for very low potentials, and for potentials up to 0·9 Daniell an empirical curve will show the relation between the two. The polarisation is complete, and no appreciable current passes through the electrometer until it is charged to a potential near that at which electrolytic action begins. The capacity of the instrument is very considerable as compared with that of the quadrant electrometer. H. C.

Aëration Currents. By C. R. A. WRIGHT and C. THOMPSON (*Proc. Roy. Soc.*, **43**, 268—273; compare Trans., 1887, 672; Abstr., 1887, 1008).—If different aëration (spongy and smooth platinum and gold) plates are placed above the same oxidisable metal in dilute sulphuric acid or aqueous potash, and left until a constant aëration is obtained, and if they then are connected together, a current is set up, which lasts with decreasing intensity for several days, and which at starting has an electromotive force equal to the difference between the electromotive forces obtained by exposing each plate to the oxidisable metal. The passage of the current electrolyses the sulphuric acid, with the result that the aëration of the positive plate is reduced, whilst that of the negative plate is increased. If the current is interrupted for some time, the plates recover their original aëration. With silver plates in sulphuric acid, acetic acid, and aqueous ammonia, a stronger current is obtained, the silver passing into solution; moreover, the amount of silver deposited in a voltameter by the current is less than that dissolved in the cell. The difference is greater with feeble than with strong currents. If the silver is opposed to a powerful oxidising agent such as platinum in nitric acid, the current produced is stronger, but the discrepancy between the quantity of silver dissolved and that deposited remains. Other metals dissolve in the same way, thus mercury opposed to an aëration plate gives mercurous sulphate. Gold in potassic cyanide gives potassium aurocyanide. Palladium behaves in a similar manner. If platinum in chromic acid is substituted for the aëration plate, gold can be dissolved in hydrochloric acid, forming aurous chloride which subsequently decomposes. H. K. T.

Electrical Conductivity of Sulphur. By E. DUTER (*Compt. rend.*, **106**, 836—837).—Sulphur is a non-conductor at all temperatures below its boiling point, but at this temperature it is possible to pass an appreciable current through the liquid. The gold electrodes which were used became covered with a deposit which is under examination. C. H. B.

Electrical Conductivity of Concentrated Nitric Acid. By E. BOUTY (*Compt. rend.*, **106**, 654—657).—The addition of water to fuming nitric acid at first causes an increase in conductivity almost proportional to the quantity of water added, and this proportionality persists through a much wider range than the increase in conductivity resulting from the addition of nitrates. From 0·076 mol. H_2O to 1·478 mol. H_2O the mean increase in conductivity is 0·456 for $\frac{1}{2}H_2O$, the unit being the conductivity of normal nitric acid, the specific resistance of which at 0° is 4·59 ohms.

When the increase in conductivity produced by salts (6·955 per equivalent) is compared with that produced by water (0·456 per equivalent), the water is less active than the salts in the ratio of 1 : 15·25, and this ratio would be still lower if the pure acid were the basis. It would seem that the electrolyte produced by the first additions of water contains a somewhat large number of molecules of water in each molecule of electrolyte.

The addition of small quantities of dehydrating substances, such as phosphoric anhydride or sulphuric acid, to the nitric acid increases its conductivity, probably owing to the formation of complex electrolytes containing both acids.

The determinations of the conductivity of concentrated nitric acid itself were not very satisfactory, owing to the action of the acid upon the vessels containing it, and consequent variations in resistance. Probably the electrolytic molecules are not the same with different degrees of dilution. A study of the phenomena of polarisation seems to indicate three distinct phases in the electrolysis, namely, the phase of the formation of the electrolyte corresponding with a composition represented by the formula $N_2O_5,4H_2O$, the E.M.F. of polarisation being 0·05 to 0·2 volt, and the increase in conductivity per equivalent of water 0·456, whilst the principal product at the cathode is nitrogen peroxide; (2) the *phase of dissociation* extending somewhat beyond the point of maximum conductivity, with an E.M.F. of polarisation of 0·6 to 0·9 volt, the product at the cathode being a complex mixture containing nitrous acid; (3) the phase extending from the point of maximum conductivity to high degrees of dilution, the E.M.F. of polarisation being from 1·6 to 1·8 volt, whilst hydrogen is the only product at the cathode. C. H. B.

Influence of the Composition of Glass on the Depression-phenomena of Thermometers. By R. Weber (*Ber.*, **21**, 1086—1096).—Tables are given showing the composition of various kinds of glass, and the depression which took place after various lengths of time. The results show that the quantity of silica present does not affect the depression, nor has the quantity of lime, which varies from 10 to 15 per cent., any appreciable effect. Neither a large amount of lime nor of silica can counteract the injurious effect caused by the presence of both potash and soda. The quantity of alumina has relatively little effect on the depression, but its presence is of use in promoting the liquefaction and thorough melting of the glass.

F. S. K.

Conduction of Heat in Liquids. By C. Chree (*Proc. Roy. Soc.*, **43**, 30—48).—A flat-bottomed dish is supported just in contact with the surface of the liquid, and into this, water at about 75° is poured, the temperature at a known depth below the surface being then ascertained at intervals by measuring the resistance of a platinum wire suspended horizontally 2·6 cm. beneath the bottom of the dish. From these measurements, the conductivity is deduced. Two series of experiments are distinguished; in the first, the water in the dish was syphoned off after a certain interval of time had elapsed; in the second, it was allowed to remain in the dish until the end of the experiment. In the first series, the conductivities measured are, the units being centimetre and minute—

For water at 18° = 0·0747.
For sulphuric acid, sp. gr. 1·054, at 20·5° = 0·0759.
For sp. gr. 1·10, at $20\frac{1}{4}$° = 0·0767.
For sp. gr. 1·14, at $19\frac{3}{4}$° = 0·0765.
For sp. gr. 1·18, at 21° = 0·0778.

From which it appears that the presence of a very considerable quantity of sulphuric acid produces an extremely small change in the conductivity for heat of water.

For carbon bisulphide at 15° = 0·0322.
For methylated spirit at 19·5° = 0·0354.
For paraffin oil at 19° = 0·0264.

The method and theory are not sufficiently accurate to allow of any value being attached to the third significant figure in the above.

The results in the second series were—

For water at 195° = 0·0815.
For methylated spirit at 18° = 0·0346.
For paraffin oil at 20° = 0·0273.
For turpentine oil at 18° = 0·0189.

The results on the whole agree with Weber's (*Ann. Phys. Chem.* [2], **10**, 103, 304, and 472). H. C.

Bibasic Glyceroxides. By DE FORCRAND (*Compt. rend.*, **106**, 665—667, and 746—749).—When sodium ethoxide and monosodium glyceroxide in molecular proportions are heated together for some time in presence of an excess of alcohol, and the liquid evaporated to dryness in a current of hydrogen at a temperature not exceeding 180°, the product contains 29·23—29·86 per cent. of sodium, and hence only about half the sodium in the ethoxide combines with the glycerol. If, however, evaporation takes place at 180—190°, decomposition is practically complete. Below 100°, the compound

$$C_3H_7NaO_3,EtOH$$

is formed; at 100—105°, or even 120° in dry hydrogen, the product is $C_3H_7NaO_3,EtONa$; at 180—190° the bibasic glyceroxide, $C_3H_6Na_2O_3$, is obtained. Potassium methoxide and monopotassium glyceroxide do not react at 180° even after several hours.

The heat of solution of *disodium glyceroxide*, $C_3H_6Na_2O_3$, at 10° is +14·48 Cal.

$C_3H_7NaO_3$ solid + Na solid = H gas + $C_3H_6Na_2O_3$ solid .... develops +29·91 Cal.
$C_3H_7NaO_3$ solid + $\frac{1}{2}Na_2O$ solid = $\frac{1}{2}H_2O$ solid + $C_3H_6Na_2O_3$ solid. .... „ +15·12 „
$C_3H_7NaO_3$ solid + NaOH solid = H_2O solid + $C_3H_6Na_2O_3$ solid .... absorbs −1·96 „

and inversely—

$C_3H_6Na_2O_3$ solid + H_2O liquid = NaOH solid + $C_3H_6Na_2O_3$ solid .... develops +3·39 „

The last result explains the instability of the compound in moist air. In the case of monosodium glyceroxide, this reaction is endothermic, and hence the compound is much more stable, and can even exist in solution in a partially dissociated condition. The reaction $C_3H_7NaO_3$ solid + EtONa solid = $C_3H_6Na_2O_3$ solid + EtOH liquid absorbs −2·08 Cal., is endothermic for the solid compounds, but becomes possible under the complex conditions of dissociation resulting from the action of heat. The following result, $C_3H_7NaO_3,EtOH$ solid + EtONa dissolved in *n*EtOH liquid = $C_3H_6Na_2O_3$ solid +

(n + 2)EtOH liquid, absorbs −16·64 Cal., explains the fact that disodium glyceroxide is only formed at a high temperature. The corresponding reaction for the monobasic glyceroxide is exothermic, and this compound is formed at the ordinary temperature.

C_3 (diamond) + H_6 gas + Na_2 solid + O_3 gas = $C_3H_6Na_2O_3$ solid, develops +239·62 Cal.

The author was unable to obtain any alcoholate of disodium glyceroxide. The residue at 120° is shown by its stability in a vacuum at 105°, and its heat of solution (+13·52 Cal. at 10°) to be the compound $C_3H_7NaO_3$,EtONa.

The heat of formation of this compound from its proximate constituents is +1·34 Cal., and in the production of disodium glyceroxide it is first formed with development of heat, but at a higher temperature decomposes with absorption of −3·5 Cal.

The heat developed by the action of a second molecule of sodium hydroxide in dilute solution on glycerol in dilute solution is only +0·22 Cal., compared with 0·515 developed by the action of the first molecule, but even this value is higher than the corresponding thermal disturbance, +0·04—0·11 Cal. in the case of alcohols. The action of sodium, sodium oxide, or sodium hydroxide on glycerol develops +14 Cal. more than the corresponding reaction with monosodium glyceroxide. The thermal disturbances resulting from the action of sodium, sodium oxide, and sodium hydroxide on monosodium glyceroxide are in each case about 2·0 Cal. lower than for the corresponding reaction with ethyl alcohol, a result which explains why, when two atoms of sodium act on a mixture of ethyl alcohol and glycerol, one atom is substituted in each compound, the bibasic glyceroxide only being formed at a high temperature.

C. H. B.

Freezing Mixture. By I. A. BACHMAN (*Amer. Chem. J.*, **10**, 45—47).—The spent acids (mixture of equal volumes of strong nitric and sulphuric acids) from Grove's battery, mixed with snow or broken ice till it forms a thin paste, gives a temperature of −30°.

H. B.

Relative Densities of Hydrogen and Oxygen. By LORD RAYLEIGH (*Proc. Roy. Soc.*, **43**, 356—363).—Regnault's method was adopted, but the globe was not cooled by ice, being simply inclosed during weighing in a wooden case, and the average temperature taken. The hydrogen was evolved from amalgamated zinc and platinum in sulphuric acid in a vacuum, the hydrogen being liberated by connecting the zinc and platinum plates, the gas was purified by potash and mercuric chloride, and dried with phosphoric anhydride. The oxygen was obtained from potassium and sodium chlorates. An important correction, overlooked by Regnault, is made in observing the compression which the globe suffers when exhausted; this the author determines by experiment, and from the theory of elastic shells. The ratio found is 15·884 (Regnault, 15·964), the difference being mainly due to the above correction. With Scott's ratio of atomic volumes 1·9965 (Abstr., 1888, 411), the value 15·912 is obtained for the ratio of atomic weights.

H. K. T.

Hydrate of Hydrogen Sulphide. By DE FORCRAND and VILLARD (*Compt. rend.*, **106**, 849—851).—The vapour-tension of the hydrate of hydrogen sulphide was determined in presence of excess of water and gas. The following table gives the differences between the tensions and 760 mm. at different temperature :—

0°	0·1°	0·6°	0·8°	0·85°	1·0°	1·2°	1·75°	2·1°
−29 mm.	−17	+20	+45	+48	+60	+70	+117	+147

2·8°	3·4°	3·8°	3·9°	4·5°	4·9°	5·2°
+222	+288	+323	+337	+403	+463	+490.

The low tension at 0° is especially noteworthy; at lower temperatures the presence of ice interferes with the determinations. The tension is, however, always below that of the atmosphere.

C. H. B.

Hydrates of Gases. By DE FORCRAND and VILLARD (*Compt. rend.*, **106**, 939—941).—According to Wroblewski, the formation of a hydrate of a gas by compression only takes place when the water holds in solution a quantity of gas corresponding with that required to produce the hydrate. It may also be supposed that at the moment of crystallisation the water contains much less gas than the hydrate, but the formation of the latter takes place with absorption of a considerable quantity of gas. The solution of a gas, and the formation of a hydrate, would then be two perfectly distinct phenomena. The second explanation only is admissible in the case of hydrates of chlorine and sulphurous anhydride, since the solutions contain a much lower proportion of these gases than the hydrates.

The apparatus used for determining the vapour-tension of the hydrate of hydrogen sulphide (preceding Abstract) was arranged so that at a pressure of 60 mm. above atmospheric pressure, it contained crystals of the hydrate, together with hydrogen sulphide and a slight excess of water. If the pressure was increased by 100 mm., and the apparatus agitated to promote the formation of more crystals, there was a considerable absorption of gas, and the pressure sank to its former value. A further increase of pressure produced a further quantity of crystals. An increase of pressure of 100 mm. does not greatly increase the solubility of the gas at constant temperature, and yet the production of the hydrate was evident from the separation of fresh crystals. When the hydrate is formed at 0°, 1 c.c. of water absorbs about 100 c.c. of gas, whereas water at +1° dissolves only 4 vols. of the gas under normal pressure. The composition of the hydrate $SH_2 + 12H_2O$ corresponds with 102 vols. of gas. Similar results were obtained with methyl chloride, and it would seem therefore that the formation of a hydrate of gas is not merely the solidification of a saturated solution, but an independent act of combination.

C. H. B.

Method for Obtaining Definite Hydrates. By E. J. MAUMENÉ and C. LIMB (*Bull. Soc. Chim.*, **48**, 777).—Crystals of oxalic acid were kept under a glass shade by the side of dried oxalic acid. After six months the crystals were titrated, and found to have a composition corresponding with the formula $C_2H_2O_4 + 2H_2O$. Crystals from the same preparation were kept in a desiccator over sulphuric acid for more than six months, when they had the composition indicated by the formula $C_2H_2O_4$. It is suggested that instead of drying substances indifferently over lime or sulphuric acid, some special substance should be selected, according to the nature of the compound to be analysed. N. H. M.

Solubility of Sulphates. By A. ÉTARD (*Compt. rend.*, **106**, 740—743).—The author's determinations, extending through a wide range of temperature, show that when the solubility of a salt is represented by a curve which expresses the weight of salt in 100 parts of solution, this curve is a right line, the angular coefficient of which varies with each salt. For one and the same salt, the coefficient changes in value at one or more points, the change being usually abrupt, although in some cases the perturbation extends through a short but measurable distance. In the majority of cases, if not in all, the sign of the coefficient changes, and the solubility decreases beyond a certain temperature. This is especially marked in the case of many sulphates, and the following coefficients have been determined by the author.

Ferrous Sulphate.—From −2° to 65°, $y = 13{\cdot}5 + 0{\cdot}3784t$; from 65° to 98° the curve of solubility is parallel with the axis of temperature; from 98° to 156°, $y = 37{\cdot}5 - 0{\cdot}6685t$. The last equation indicates that the salt should be insoluble at 156°, and this conclusion has been verified experimentally.

Cadmium Sulphate.—From 0° to 68°, $y = 35{\cdot}7 + 0{\cdot}2160t$; from 68° to 200°, $y = 50{\cdot}6 - 0{\cdot}3681t$. At 200° the salt dissolves only to the extent of 2 per cent., and at 215° it is insoluble.

Magnesium Sulphate.—From 0° to 123°, $y = 20{\cdot}5 + 0{\cdot}2276t$; from 123° to 190°, $y = 48{\cdot}5 - 0{\cdot}4403t$. The salt should become insoluble at 233°, but this was not verified. A solution saturated at +15° becomes turbid at 178°, and deposits a hydrate in porcelain-like crusts.

Lithium Sulphate.—From −20° to −10·5°, $y = 18{\cdot}5 + 0{\cdot}8421t$; from −10·5° to 100°, $y = 26{\cdot}5 - 0{\cdot}0274t$.

Rubidium Sulphate.—From 0° to 49°, $y = 26{\cdot}5 + 0{\cdot}2959t$; from 49° to 170°, $y = 41{\cdot}0 + 0{\cdot}0661t$.

Potassium Selenate.—From −20° to 100°, $y = 52 + 0{\cdot}0250t$.

Selenious Anhydride.—From −3° to 36°, $y = 45{\cdot}0 + 07692t$.

In several cases the observations are complete, since they extend from the point of congelation of the solution to the temperature at which the salt again becomes insoluble. The point of congelation corresponds with a certain ratio between the salt and the water. As the temperature rises, the change in presence of an excess by the salt is analogous to etherification. A certain quantity of water is set free, and dissolves a further quantity of the salt, and this change continues as the temperature rises, the solubility of the salt increasing by reason of the dehydration of the original system up to the point of maximum solubility. A change analogous to saponification then sets in, and as the temperature rises the salt is gradually deposited, the water playing an increasing part in the establishment of equilibrium until at a certain temperature the water completely displaces the salt, and the latter becomes insoluble. C. H. B.

Laws of Chemical Equilibrium. By P. DUHEM (*Compt. rend.*, **106**, 846—849).—A continuation of the discussion with Le Chatelier. C. H. B.

Raoult's Method for the Determination of Molecular Weight and on Acetoxime. By K. AUWERS and V. MEYER (*Ber.*, **21**, 1068—1070).—The authors suggest that in Raoult's method glacial acetic acid should always be employed as the solvent, and neither benzene nor water.

Beckmann's determinations of the molecular weight of oximes (this vol., p. 409) are probably wrong, owing to his having used benzene. Experiments made by the authors on acetoxime show that when glacial acetic acid is used, the results obtained agree with the formula C_3H_7NO.

When it is absolutely necessary to make use of water or benzene, the results are of value only after having first made experiments with a compound of strictly analogous constitution, the molecular weight of which is known. F. S. K.

Molecular Weight of Oximes. By E. BECKMANN (*Ber.*, **21**, 1163—1164).—The conclusions arrived at by the author with reference to the molecular weights of the oximes (this vol., p. 409) were based on the lowering of the freezing point of benzene, which was employed as the solvent for the various oximes examined. When, however, acetic acid is used, results are obtained which, in the case of acetoxime and benzaldoxime, are in agreement with the molecular weights usually adopted. The molecular weights of these oximes as determined by the lowering of the vapour-tension of their ethereal solutions are also those ordinarily assumed. W. P. W.

Apparatus for Fractional Distillation. By E. CLANDON and E. C. MORIN (*Bull. Soc. Chim.*, **48**, 804—811).—The apparatus is intended for the distillation of large amounts of liquids, 100 litres for example. It is made entirely of copper. For description of the apparatus the original paper, in which sketches are given, must be referred to. N. H. M.

Apparatus for Fractional Distillation. By T. H. NORTON and A. H. OTTEN (*Amer. Chem. J.*, **10**, 62—69).—The apparatus is constructed on the principle of Tcherniac's "déverseur" for the separation of froth during distillation (*Wurtz Dict.*, *Supp.*, 597), so that the vapours are not washed through the condensed liquid, but are at once separated. The apparatus is decidedly fragile, and on the whole yields no better results than the fractionating tubes of Linnemann and Hempel. H. B.

Pressure Tubes. By H. N. WARREN (*Chem. News*, **57**, 155).—The author adopts the following plan to make glass tubes resist internal pressure at high temperatures. For temperatures ranging from 200° to 400°, the sealed tube is enclosed in a copper tube, the intervening space being closely packed with magnesia. For higher temperatures, a wrought-iron external tube is used with sand as the packing material. D. A. L.

Turbine for Laboratory Purposes. By H. RABE (*Ber.*, **21**, 1200—1201).—The author has devised a simple form of turbine which, when connected with the water service of a laboratory, is capable of providing the motive power required for mechanical stirring.
W. P. W.

Lecture Apparatus for making Sulphuric Anhydride. By W. R. HODGKINSON and F. K. LOWNDES (*Chem. News*, **57**, 193).—The apparatus consists of an inverted bell-jar. The smaller opening is fitted with a caoutchouc stopper carrying a wooden rod to which a piece of stout platinum wire is attached supporting some spongy platinum in the centre of the jar. The large opening is firmly closed by a piece of wood, through which two tubes (one for oxygen, the other for sulphurous anhydride) pass and terminate close to the platinum sponge which just previous to use has been heated in a bunsen flame. Sulphuric acid forms rapidly when the two gases are made to impinge on the hot spongy platinum. D. A. L.

Inorganic Chemistry.

Relative Values of the Atomic Weights of Hydrogen and Oxygen. By J. P. COOKE and T. W. RICHARDS (*Amer. Chem J.*, **10**, 81—110; comp. Lord Rayleigh, this vol., p. 643).—The only direct determinations of this ratio that are independent of all other considerations and determinations are those of Dumas and of Erdmann and Marchand, and both these contain possible errors and uncertainties that are so great as to render the results obtained worthless for deciding between the numbers 15·96 and 16·00 as the atomic weight of oxygen.

The principal source of possible error is that the amount of hydrogen is determined by the difference of the weights of water and of oxygen, and the combined errors of these two determinations are then exaggerated because of the comparative smallness of the number that expresses the hydrogen. In the present determination the hydrogen was actually weighed. The globe used was counterbalanced by a similar one, and its weight could be satisfactorily determined to one-tenth of a milligram; it held nearly 5 litres, and was provided with glass stopcocks. After exhausting to 1 mm. it was weighed, filled with hydrogen, and again weighed.

In the first series of experiments, the hydrogen was prepared from almost pure zinc and hydrochloric acid; the dissolved air was removed from the dilute acid by boiling in a stream of hydrogen and preserving it in an atmosphere of hydrogen. The gas was purified by passing through a 5-foot tube of potash solution (necessary to remove sulphur dioxide), then dried by calcium chloride, sulphuric acid, and phosphorus pentoxide; wherever possible, joints were made by sealing together the glass tubes, all others were protected by a cement composed of equal parts of pitch and gutta-percha. In the second series of experiments, the hydrogen was prepared from hydrochloric acid and a semi-fluid amalgam of zinc; the amalgam could be connected externally with a platinum plate immersed in the acid, and by making connection and interposing a varied electrical resistance, or by connecting with a battery, the hydrogen could be obtained at any desired speed. The gas was purified as before. In the third series, the hydrogen was prepared by dissolving sheet aluminium in pure aqueous potash. The long potash washing tube was dispensed with, but the gas dried as before. The globe was then connected with the rest of the apparatus that had previously been filled with nitrogen. The apparatus consisted firstly of heated tubes containing copper to remove oxygen from the air current, copper oxide to remove hydrogen occluded by the copper or organic matter in the air; secondly, drying tubes containing potash, calcium chloride, sulphuric acid, and phosphorus pentoxide; thirdly, the weighed globe containing hydrogen; fourthly, tube containing heated copper oxide; fifthly, the apparatus for collecting the water, namely, an empty tube, strong sulphuric acid, and phosphorus pentoxide; and, lastly, an apparatus for regulating the suction of air through the whole apparatus. The gas current was rapid the whole time; after the first half hour, more than nine-tenths of the hydrogen was burnt, and after the first hour the first tube containing copper was removed, all possibility of an explosion being at an end, and air instead of nitrogen was drawn through the apparatus. By this means the whole apparatus is left in its initial condition, namely, the reduced copper oxide is reoxidised completely, thus avoiding all error due to occlusion of hydrogen, and the condensing tubes are left also full of ordinary air. The actual experiment lasted altogether about eight hours, which time was shown to be amply sufficient. The weight of hydrogen burnt averaged 0·42 gram. The results obtained are—

	Maximum.	Minimum.	Average.	Error.
First series (5)....	15·977	15·937	15·954	±0·0048
Second series (5)..	15·962	15·942	15·953	±0·0022
Third series (6) ..	15·967	15·937	15·952	±0·0035
Average of the three series			15·953	±0·0017
Dumas obtained			15·960	±0·0070

or, having regard only to the substances actually weighed, the composition of water is :—Oxygen (Dumas) 88·864 ± 0·0044, and hydrogen (Cooke and Richards) 11·140 ± 0·0011; total 100·004.

The results recently given by Keiser (Abstr., 1887, 1078) namely, 15·873, 15·897, and 15·826 are not concordant, and are vitiated by varying impurities in the gas used. H. B.

Atomic Weight of Oxygen. By E. W. MORLEY (*Amer. Chem. J.*, **10**, 21—26).—It is pointed out that the conclusion drawn by Scott (this vol., p. 411) as to the ratio in which hydrogen and oxygen combine is not warranted by his experimental method, more particularly because the amount of impurities in the hydrogen and in the oxygen used were not separately estimated. Methods are proposed by which these impurities can be estimated and allowed for, and also new methods for effecting the synthesis of water in the most exact manner. H. B.

Oxidation of Solutions of Sulphurous Anhydride and Sulphites. By I. A. BACHMAN (*Amer. Chem. J.*, **10**, 40—41).—Solutions of normal potassium, sodium, and ammonium sulphites were completely oxidised in three weeks, whilst sulphurous acid had lost by volatilisation and oxidation three quarters of its strength, and acid ammonium sulphite had only lost about 45 per cent. All the solutions contained 10 grams of sulphurous anhydride per litre, were kept in open bottles, and shaken twice daily. H. B.

Sulphites. By A. RÖHRIG (*J. pr. Chem.* [2], **37**, 217—253).—The author has revised the work of Muspratt (*Annalen*, **50**, 259), Rammelsberg (*Ann. Phys. Chem.*, **67**, 245), and others, and has fully described the sulphites of lithium, thallium, the alkaline earths, lead, magnesium, zinc, cadmium, aluminium, uranium, bismuth, iron, chromium, manganese, nickel, cobalt, and tin, with the result, in general, that the older observations are confirmed. Attempts to obtain the two isomeric salts $NaSO_2\cdot OK$ and $KSO_2\cdot ONa$ were not successful, only one potassium sodium sulphite being formed under any circumstances. G. T. M.

Simple Formation of Thiosulphates. By E. DONATH and F. MÜLLNER (*Dingl. polyt. J.*, **267**, 143).—This method is based on the oxidation of metallic sulphides in aqueous solution by boiling with manganese dioxide. D. B.

New Sulphur Oxy-acid. By A. VILLIERS (*Compt. rend.*, **106**, 851—853).—Sodium thiosulphate is mixed with a quantity of water insufficient for complete solution, and the mixture is saturated with sulphurous anhydride. If any salt now remains undissolved more water is added, and the mixture is again saturated with the gas. A yellow solution is obtained, and if this is evaporated immediately in a vacuum, it evolves sulphurous anhydride, and, if the temperature does not exceed 0°, only sodium thiosulphate is obtained from the residue. If the solution is allowed to remain at the ordinary temperature for two or three days, it will then absorb more sulphurous anhydride, and if after saturation it is allowed to remain for a day or two and is then evaporated in a vacuum over sulphuric acid, it yields brilliant, white, brittle, anhydrous prisms of the composition $Na_2S_4O_6$. When these crystals are dissolved in water and evaporated as before, the hydrate $Na_2S_4O_6 + 2H_2O$ is obtained in soft, waxy crystals arranged in nodules.

If the mother-liquor from the first crystals is concentrated, it yields small crystals of the trithionate $Na_2S_3O_6 + 3H_2O$, which has not previously been crystallised. The formation of these salts is represented by the following equations:—$2Na_2S_2O_3 + 5SO_2 = 2Na_2S_4O_6 + S$ and $2Na_2S_2O_3 + 3SO_2 = 2Na_2S_3O_6 + S$. At a low temperature very little sulphur is actually liberated, and it seems to unite with the thiosulphate, forming a salt of the composition $Na_2S_3O_3$.

The salt $Na_2S_4O_8$ may be regarded as a derivative of dithiopersulphuric acid, H_2O,S_2O_7,S_2. C. H. B.

Formation of Crystallised Selenates in the Dry Way. By L. MICHEL (*Compt. rend.*, **106**, 878—881).—The selenates described were prepared by fusing the chloride of the particular metal with an alkaline selenate and some sodium chloride, cooling very slowly, and extracting with water. The insoluble residue is a mixture of crystals with a crystalline powder, and if the latter is mixed with sodium chloride and heated until the greater part of the solvent is volatilised, crystals several millimetres in length are obtained.

Barium selenate forms colourless or bluish-white crystals with a vitreous lustre; hardness 3 to 4; sp. gr. 4·75. They are rhombic octahedra elongated along the greater diagonal, and are frequently arranged in groups parallel with *h'*. In form and optical property, they are identical with barytes.

Strontium selenate forms rhombic prisms of sp. gr. 4·23, closely resembling the crystals of celestine from Lake Erie, and precisely similar to celestine in crystallographic and optical properties.

Calcium selenate forms colourless or milk-white rectangular lamellæ of sp. gr. 2·93; hardness 3·5. It melts before the blowpipe without exfoliation, and is only slightly soluble in water or nitric acid. Hydrochloric acid attacks it slowly with evolution of chlorine. Optical examination shows that its properties are very similar to those of anhydrite.

Lead selenate cannot be obtained in the same way, but a mixture of the amorphous selenate, lead nitrate, and sodium nitrate yields small rhombic prisms with all the characters of anglesite.

Measurements of the angles of the crystals, &c., are given in the paper. From the results it follows that the artificially prepared anhydrous selenates of barium, calcium, strontium, and lead, are isomorphous with one another and with the corresponding natural sulphates. C. H. B.

Arsenic Nitride. By I. A. BACHMAN (*Amer. Chem. J.*, **10**, 42—44).—When a tube containing silver cyanide and arsenious oxide is heated at 300—400°, a dark-brown substance is formed as a coating over the arsenious oxide crystals. The mixture contains about 2 per cent. of nitrogen with only a trace of carbon, and is probably the hitherto unknown arsenic nitride. H. B.

Decomposition of Ammonium Chloride by Phosphoric Acid. By K. W. JURISCH (*Dingl. polyt. J.*, **267**, 424—431).—The author has investigated Witt's process (*Ger. Pat.* 34395, May, 1885) for the preparation of hydrochloric acid, and ammonia from ammonium chloride by decomposition with phosphoric acid. The method is intended to replace the troublesome distillation of the mother-liquors by means of lime, and to recover the chlorine lost in the calcium chloride. The separation of the ammonium chloride is effected either by evaporation to dryness and sublimation, or by fractional crystallisation. The author found that of 12 mols. of phosphoric acid employed, 8 mols. are taken up and 4 mols. remain as free acid, half being orthophosphoric acid, the remainder pyrophosphoric acid. In order to complete the decomposition at a low temperature without volatilising the ammonium chloride, an excess of phosphoric acid is required, hydrochloric acid only being expelled. On subsequently increasing the temperature, from 63 to 86 per cent. of ammonia is given off. The residue which consists of metaphosphoric acid with some ammonium metaphosphate may be used for the decomposition of a fresh portion of ammonium chloride, so that it is possible to decompose ammonium chloride in succession by the same quantity of phosphoric acid without loss of acid. Owing to the difficulty of obtaining a material for lining the furnace or other vessel capable of resisting the action of fused phosphoric acid, the application of the process on a large scale has hitherto been impossible. According to Brunner, Mond, and Co., even platinum is so energetically attacked by the acid that it cannot be employed for the heating vessel.

D. B.

Oxidation of Silver. By H. LE CHATELIER (*Bull. Soc. Chim.*, **48**, 342—345).—When pure precipitated silver is heated in oxygen at 300° under a pressure of 15 atmospheres it is slowly oxidised. The oxidation could not be completed, and the largest amount of silver oxidised was 50 per cent. The decomposition of silver oxide at the same temperature was found to be extremely slow; the pressure increased for three days, and then remained constant at about 10 atmospheres. The tension at which the oxide decomposes at 300°, is, therefore, between 10 and 15 atmospheres. At 400—450° silver oxide decomposes rapidly. N. H. M.

Alloys of Calcium and Zinc. By T. H. NORTON and E. TWITCHELL (*Amer. Chem. J.*, **10**, 70—72).—Following the directions of Caron (*Compt. rend.*, **50**, 547) calcium chloride, zinc and sodium were heated together, but the alloys obtained did not contain more than 2·3 to 6·4 per cent. of calcium, instead of 10 to 15 per cent. as reported. The poorest alloy melted at 360°, the same temperature as zinc, but it is remarkable that the richer alloys melted at as high a temperature as 640°. They do not decompose water, or oxidise at ordinary temperatures in the air, and the zinc cannot be removed by volatilisation in a current of hydrogen without losing considerable quantities of calcium. H. B.

Action of Metallic Oxides on Solutions of Zinc and Manganese Chlorides. By G. ANDRÉ (*Compt. rend.*, **106**, 854—856).—The finely divided oxides were heated or boiled with water and zinc chloride until they were completely dissolved, or until no further change was observed, and the solutions were slowly cooled.

Zinc chloride and yellow mercuric oxide yield the white, amorphous zinc oxychloride, $2ZnCl_2,3ZnO + 11H_2O$, which when washed with alcohol and dried on paper, changes to $ZnCl_2,4ZnO + 6H_2O$. It is remarkable that mercuric oxide yields only a zinc oxychloride, since with magnesium chloride it forms a double oxychloride (Abstr., 1887, 446 and 447).

Lead oxide and zinc chloride yield brilliant, white, slender needles, which contain an almost constant proportion of chlorine, whilst the proportions of lead and zinc vary. In most cases, they are a compound of $ZnCl_2,3ZnO$ with $ZnCl_2,PbO$. The latter compound may be regarded as lead oxychloride in which the zinc lead chloride has been replaced by the zinc salt.

Cupric oxide and zinc chloride yield a green powder of the composition $Zn_3Cu_6Cl_4O_6 + 6H_2O$, or supposing it to be derived from the well-known oxychloride, $ZnCl_2,3ZnO$, it may have the constitution $(ZnCl_2,ZnO,2CuO)(ZnCl_2,3CuO) + 6H_2O$. Cupric oxide and manganese chloride produce an apple-green powder, $MnCl_2,3CuO + 3H_2O$, which may be regarded as the unknown oxychloride, $MnCl_2,3MnO$, in which cupric oxide has replaced manganous oxide. It is not affected by boiling with a solution of manganous chloride.

Lead oxide and manganese chloride yield lead chloride only, but if the mother-liquor is poured into cold water, the compound $2PbCl_2,2PbO + 3H_2O$, is obtained as a flocculent precipitate.

Attempts to obtain ammoniacal oxychlorides in which the base of the oxide was different from the base of the chloride were unsuccessful.

C. H. B.

Supposed Dissociation of Zinc Oxide: Condition of the Atmosphere within a Platinum Vessel heated by a Gas Flame. By H. N. Morse and W. M. Burton (*Amer. Chem. J.*, **10**, 148—153).—When zinc oxide is heated for many hours in platinum vessels in a muffle furnace to a temperature above the melting point of steel, it does not lose weight, nor is the crucible in any way altered; but when heated over a gas-lamp or blowpipe there is a constant loss of weight, as has been noticed by Erdmann and by Marignac, who ascribed the loss to dissociation of the oxide. The explanation is, however, disproved by the above stated behaviour of zinc oxide in a muffle furnace, and by the fact that the atmosphere within a platinum vessel strongly heated by a gas flame always contains free hydrogen, which reduces the zinc oxide. The hydrogen is produced by the dissociation of the water produced in the cooler parts of the flame, and is then occluded by the platinum, and so passes through the crucible. A platinum tube connected with a gas burette, the whole holding 130 c.c. of air, was heated with a blast-lamp for 1, 2, 3, and 4 hours, when 54, 88·5, 98·1, and 100 per cent. of the oxygen of the confined air disappeared, and in the last two cases, moreover, 2·4 and 2·7 c.c. of free hydrogen were present, so that at least 22·8, 44, 44·5, and 48·2 c.c. of hydrogen must have passed through the platinum. This amount is increased from 22·8 c.c. to

28·5 c.c. by slightly diminishing the internal pressure by 30 mm., and is decreased to 20·9 by increasing the pressure by the same amount. Similar results were obtained by using an ordinary bunsen burner. In all cases only the outer or oxidising flame was allowed to touch the tube. The bearing of these facts on the ignition of precipitates in platinum vessels is obvious.

H. B.

Colloidal Cadmium Sulphide. By E. Prost (*Chem. Centr.*, 1888, 32, from *Bull. Acad. Belg.* [3], **14**).—Colloidal cadmium sulphide can be prepared by completely precipitating an ammoniacal solution of cadmium sulphate with hydrogen sulphide, washing the sulphide with water by decantation, suspending the precipitate in water, and submitting it to a slow stream of hydrogen sulphide, the precipitate becomes first flocculent, then milky, and finally disappears entirely. The solution is then boiled until lead paper shows the absence of hydrogen sulphide. The solution is a beautiful golden-yellow by transmitted and fluorescent by reflected light. The composition of the dissolved substance is CdS. Dilute solutions remain unchanged for a long time. A solution containing 4 grams of sulphide to the litre remained clear many days, but another solution containing 11 grams to the litre coagulated in 24 hours. The following are the results of experiments on the coagulation of the colloidal sulphide.

(1.) There is no relation between the molecular weight of acid and salt and their coagulating activity. (2.) The coagulating power of salts is determined by the metal they contain. The greater the valency of the metal they contain, the greater their energy. The influence of the acid is generally not marked. Potassium sulphate coagulates in dilutions of 1 in 1666 parts, aluminium sulphate in dilutions of 1 in 232,558 parts. (3.) Among the alums, those of the triad metals are most active. (4.) The coagulating power of acid salts appears to be greater than that of normal salts. (5.) Cadmium salts are very active in coagulating the sulphide, 1 part in 250,000 of cadmium sulphate and 1 part in 285,714 of cadmium nitrate sufficing.

Most of these results agree with Schulze's results with arsenic and antimony sulphides. The concentration of the colloidal sulphide is without influence on the manner in which it coagulates.

J. P. L.

Action of Heat on Oxides and Salts of Manganese. By A. Gorgeu (*Compt. rend.*, **106**, 743—746).—Anhydrous manganous oxide heated rapidly and strongly yields the red oxide, but if care is taken to avoid incandescence, and the oxide is heated to dull redness until its weight is constant, the sesquioxide is obtained. The oxidation at 200° to 430° of the manganous oxide prepared at a high temperature ceases with the formation of the oxide $MnO_2,4MnO$, but if the manganous oxide was prepared at a dull red heat and is oxidised for the same time below 430° it yields a higher oxide, which, however, contains less oxygen than the sesquioxide. The action of air at 200—430° on manganous oxide prepared below 400° could not be determined directly, because the oxide is pyrophoric either at the ordinary temperature or at 140°, but the conclusion just stated was deduced from the behaviour of the carbonate and oxalate.

The red oxide, even if prepared at a red heat, will oxidise in the air after being finely powdered, the oxidation taking place more rapidly and at a lower temperature the lower the temperature at which the oxide was produced. Trimanganese tetroxide prepared at a red heat never yields an oxide higher than the sesquioxide, and the time required to obtain this result is longer the higher the temperature at which the original oxide was formed. Samples of this oxide prepared at 250—300° and heated at 200—430° yield the oxide $3MnO_3,2MnO$, but these are the only exceptions to the formation of the sesquioxide. The sp. gr. of the more easily oxidised varieties of trimanganese tetroxide is usually below 4·70, whilst that of the varieties which oxidise with difficulty is generally above 4·8.

In making estimations of manganese, it is advisable to heat the oxide to bright redness for a few minutes. Under these conditions, the absorption of oxygen during cooling is absolutely *nil*.

Manganese sesquioxide prepared at a dull red heat undergoes no alteration in the air at a temperature below that at which it was formed. The natural sesquioxide, Mn_2O_3,H_2O, however, oxidises easily at 275—295°, and yields the pure dioxide. It follows that the sesquioxide only oxidises in presence of air when it has been produced at a low temperature.

The oxides formed by the action of heat on manganous carbonate, oxalate, tartrate, or acetate are similar to those obtained from manganous oxide formed at the temperature at which the particular salt decomposes.

Manganous chloride, bromide, iodide, or fluoride decomposes when heated to redness in presence of moist air, and eventually yields the crystallised oxide Mn_3O_4 below a red heat. The iodide decomposes at 250°, and yields at first the oxide Mn_3O_4, but this is converted into the sesquioxide by heating to dull redness, or into the oxide $3MnO_2,2MnO$ below 430°. The bromide forms trimanganese tetroxide, and afterwards the sesquioxide; the fluoride forms only the sesquioxide. The chloride at a dull red heat yields crystals of the oxychloride $2Mn_2O_3,MnCl_2$.

The oxides obtained, in addition to the four well-known oxides, are $MnO_2,4MnO$ and $3MnO_2,2MnO$, but these are amorphous, and it is possible that they are merely mixtures and not distinct species.

C. H. B.

Action of Iodine on Iron. By G. Fleury (*J. Pharm.* [5], **16**, 529—530).—The two elements in presence of water react with evolution of a considerable amount of heat. If the temperature is kept down to about 15°, the action soon ceases, although the iodine dissolves completely and strongly colours the liquid. On filtering, the residue consists of black iron without any peroxide. A different result follows if the mixture is heated to boiling, the red coloration quickly disappears, and a notable quantity of ferric oxide is found in the residue. To dissolve all the iron, a large excess of iodine is necessary, and conversely a large excess of iron is required to convert all the iodine into ferrous iodide. The foregoing is explained by supposing that the ferric iodide first formed is decomposed by the heat, yielding ferric oxide and hydriodic acid; the latter then acts on the free iron forming ferrous iodide. Hence the mutual action of the two elements is not so simple as is usually supposed. J. T.

Double Salts of Sesquichlorides with other Metallic Chlorides. By G. NEUMANN (*Annalen*, **244**, 328—349).—The following double salts were prepared by adding a metallic chloride to a hot, strong solution of ferric chloride in hydrochloric acid (sp. gr. 1·19): $4KCl,Fe_2Cl_6 + 2H_2O$, reddish-brown octahedra and rhombic dodecahedra; $4NH_4Cl,Fe_2Cl_6 + 2H_2O$, dark-red crystals; $4RbCl,Fe_2Cl_6 + 2H_2O$, small, yellow crystals; $2MgCl_2,Fe_2Cl_6 + 2H_2O$, large, brownish-yellow, hygroscopic crystals; $2BeCl_2,Fe_2Cl_6 + 2H_2O$, small orange crystals.

The double chromic chlorides can be prepared by adding a relatively small quantity of the chloride of an alkali to a solution of chromic chloride (dry) in 96 per cent. alcohol. The solution is saturated with hydrogen chloride and boiled; on cooling, the double salts are deposited in crystals. Those described are $4KCl,Cr_2Cl_6 + 2H_2O$; $4RbCl,Cr_2Cl_6 + 2H_2O$; $4NH_4Cl,Cr_2Cl_6 + 2H_2O$; $2MgCl_2,Cr_2Cl_6 + 2H_2O$; $2BeCl_2,Cr_2Cl_6 + 2H_2O$; $6TlCl,Cr_2Cl_6$.

Double aluminium chlorides could not be obtained except in one isolated experiment, which yielded beautiful crystals of the composition $4KCl,Al_2Cl_6 + 2H_2O$.

The thallic double salts are prepared by passing chlorine into a solution of thallic chloride and the alkali chloride in strong hydrochloric acid. The anhydrous salts crystallise in rhombic plates, and the hydrated salts belong to the quadratic system. The following salts were prepared:—$2TlCl,Tl_2Cl_6$; $6TlCl,Tl_2Cl_6$; $6NH_4Cl,Tl_2Cl_6$; $6RbCl,Tl_2Cl_6$; $3BeCl_2,Tl_2Cl_6$; $6KCl,Tl_2Cl_6 + 4H_2O$; $6NH_4Cl,Tl_2Cl_6 + 4H_2O$. W. C. W.

Ammoniacal Derivatives of Nickel Salts. By G. ANDRÉ (*Compt. rend.*, **106**, 936—939).—A cold solution of nickel chloride is saturated with ammonia, gently heated until the crystalline precipitate dissolves, and allowed to cool, when it deposits transparent, violet octahedra of the composition $2(NiCl_2,6NH_3) + H_2O$. The crystalline precipitate has the same composition, and the compound can also be obtained in large, opaque octahedra containing 3 mols. H_2O, by passing ammonia into a solution of ammonium chloride containing nickel oxide in suspension. When boiled with water, or heated in sealed tubes at 200°, the ammoniacal compound yields amorphous nickel oxide.

If a solution of nickel chloride is gradually mixed with a limited quantity of dilute ammonia and the precipitate washed with cold water and dried at 100°, it has the composition $NiCl_2,8NiO + 13H_2O$.

When ammonia is passed for a long time into a cooled solution of nickel sulphate and the liquid gently heated, large, deliquescent, pale-violet needles of the composition $2NiSO_4,10NH_3 + 7H_2O$ separate on cooling. A sulphate of the usual type, $NiSO_4,4NH_3,2H_2O$, was described by Erdmann and Laurent.

If ammonia is passed into a solution of ammonium sulphate containing nickel oxide in suspension in the proportion of 1 mol. of oxide to 2 of the salt, and the liquid is heated and allowed to cool, large, blue, rhombic prisms of the salt $2[NiSO_4,(NH_4)_2SO_4,6NH_3] + 3H_2O$ are obtained. The same compound is obtained on passing ammonia into a solution of the two sulphates in equivalent proportions.

The salt $2[Ni(NO_3)_2,6NH_3] + 3H_2O$ is obtained by passing ammonia into a solution of nickel nitrate, or into a solution of ammonium nitrate containing nickel oxide in suspension. The nitrate described by Erdmann was not obtained. Nickel, like cadmium, forms only one ammoniacal nitrate, and the two salts are analogous, but differ from the ammoniacal nitrates of copper and zinc. C. H. B.

Metallurgy of Bismuth. By E. Matthey (*Proc. Roy. Soc.*, **43**, 172—173).—Instead of the usual wet method, the author removes copper from bismuth by fusion with bismuth sulphide, the copper displacing the bismuth in the sulphide. By this means 90 per cent. of pure metal can be obtained from the crude material, the mixed sulphides being also suitable for reduction and resmelting. Other impurities, arsenic, antimony, lead, &c., are first removed (comp. Abstr., 1887, 900). The bismuth operated on contained 0·1—1·0 per cent. copper. H. K. T.

Separation of Platinum from Rare Metals. By H. Pirngruber (*Chem. Centr.*, 1888, 84—85, from *Eng. and Min. J.*, **44**, 256).—The ores are first treated with chlorine-water to remove any gold, and then with aqua regia under pressure. Osmium and iridium and some of the rhodium and ruthenium remain undissolved. The solution is boiled with soda and treated with alcohol and potassium chloride; after acidifying with hydrochloric acid, potassium platinochloride separates, from which the platinum is obtained by reduction. The metals remaining in solution are precipitated with zinc or iron.

The insoluble residue left on treatment with aqua regia is heated in a porcelain retort in a stream of air or oxygen; osmium oxidises and volatilises as OsO_4, which decomposes into the metal and oxygen at a red heat. The residue in the retort and the metals obtained by precipitation with zinc or iron are united and melted with four times their quantity of zinc under a covering of zinc chloride; the alloys are heated with hydrochloric acid until palladium begins to dissolve, and the solution turns brown. The black residue left after decanting off the liquid is boiled with aqua regia: part of the rhodium and ruthenium remains undissolved. From this solution, after treatment with soda, the palladium is precipitated as iodide with potassium iodide, avoiding excess; the iodide is reduced with hydrogen, the metal dissolved in concentrated nitric acid, and reprecipitated as the double salt with potassium chloride, which is again reduced with hydrogen.

The solution from which the palladium has been separated is reduced with hydrogen, when all the metals, with the exception of iridium, are precipitated. The solution is filtered and the filtrate oxidised by boiling with aqua regia. The iridium is precipitated with potassium chloride as potassium iridiochloride in dark-red cubes; the metal is obtained by simply heating the compound.

The precipitate of metals obtained by reduction with hydrogen is mixed with the rhodium and ruthenium and treated with zinc and hydrochloric acid. The black powder is then heated with barium chloride in a stream of chlorine, any osmium that may still remain will be volatilised as $OsCl_2$. The residue, a barium rhodiochloride, is dissolved in water and the barium removed with sulphuric acid. On the addition of sodium hydrogen sulphite to the filtrate, a yellow salt ($3Na_2O,Rh_2O_3,6SO_2$) is precipitated. This salt when treated with boiling sulphuric acid and the excess of acid driven off, is converted into the double salt $Na_2O,Rh_2O_3,4SO_3$, which is insoluble in acids and water, but is decomposed by potash, the hydroxide being formed. If this is dissolved in hydrochloric acid and reduced with hydrogen, the metal is obtained.

To obtain ruthenium, the osmium-iridium residue is melted with zinc and treated with hydrochloric acid as above. The insoluble metallic powder is then boiled with potash and potassium chromate, and subsequently heated with sodium sulphate after the addition of an excess of potash; only ruthenium is precipitated. J. P. L.

Mineralogical Chemistry.

Sellaïte. By A. SELLA (*Chem. Centr.*, 1887, 1236, from *Rend. Acc. Lincei* [4], **3**, 529—530).—The author has met with sellaïte in anhydrite found in the Gebroulaz Glacier near Montiers, in Savoy. Strüver determined the form of the prismatic sellaïte crystals and found them on analysis to be composed of magnesium fluoride. Cossa also, from magnesium fluoride, prepared artificial sellaïte which corresponded with the natural product. The author now confirms the composition. Albite, fluorite (in cubo-dodecahedrons), quartz, and dolomite in beautiful tabular, transparent crystals (some forms hitherto undescribed) were found with this mineral.

Sellaïte occurs there in anhydrite which changes to gypsum, and contains sulphur and dolomite interstratified with it. J. P. L.

Proustite containing Antimony. By H. A. MIERS and G. T. PRIOR (*Min. Mag.*, **7**, 196—200).—A magnificent specimen of proustite from Chañarcillio, Chili, has been recently acquired for the British Museum. It is a mass of lustrous crystals, measuring 3 inches by $2\frac{1}{2}$ inches, and 3 inches in height. The forms observed were $-\frac{1}{2}R$, $-2R$, $R3$, $-2R\frac{5}{3}$. The rhombohedron angle was found on measurement to be 72° 12′. On analysis the mineral was found to contain 13·85 per cent. of arsenic and 1·41 per cent. of antimony. Its sp. gr. is 5·64. The analyses made prove that the antimony is very unevenly distributed throughout the specimen. It is probably present in smaller quantities in the better crystallised parts, and possibly the surface of the crystals contains no antimony. It is certain that in the crystals analysed the presence of more than 1 per cent. of antimony has no appreciable effect on the rhombohedral angle.

B. H. B.

Copper Antimonide. By A. Laist and T. H. Norton (*Amer. Chem. J.*, **10**, 60—62).—This new mineral comes from near Mytilene in Eastern Asia Minor, and is found in large quantity. It is lustrous, silver-white, tarnishes easily, shows no crystalline structure, is very brittle, and has a hardness of 4 to 5. Its melting point lies between that of antimony glance and of natrolite. Its specific gravity is as high as 8·812. Analysis gives—

Cu.	Sb.	Total.
73·37	26·86	100·23

a composition lying between that required by the formulæ Cu_5Sb and Cu_6Sb, and corresponding closely with Ag_6Sb, the only known native antimonide besides Ag_3Sb. A very similar substance is obtained by fusing the ingredients in the above proportions. The mineral is termed *horsfordite*.

H. B.

Varvacite. By P. H. Walker (*Amer. Chem. J.*, **10**, 41—42).—The sample was from Austinville, Wythe Co., Va., U.S., and occurs imbedded in psilomelane and ferruginous clay in radiating fibrous crystals.

MnO_2.	MnO.	BaO.	H_2O.	SiO_2.	Fe_2O_3 and Al_2O_3.
68·86	7·51	14·42	5·08	1·98	2·23 = 100·08

H. B.

Occurrence of Oxide of Cobalt. By H. Rössler (*Dingl. polyt. J*, **267**, 518—520).—The ancient Saxon and Swedish ores which contain cobalt in combination with arsenic and were formerly almost exclusively used for the manufacture of cobalt, have for some time ceased to meet the increasing demand for this metal, by far the largest proportion being now extracted from the manganesiferous brown iron ores of New Caledonia. These contain about ·2 per cent. of cobalt and the same quantity of nickel. Cobalt is also present in considerable quantity in the black copper ores of the Spanish province of Leon. It occurs also in iron ores and in numerous manganese ores. Its occurrence in porphyry at Imsbach near the Donnersberg, in the Palatinate of the Rhine, is of interest, inasmuch as a fissure about one metre in width traverses the rock which is filled up with a loose mass of ferric and manganic oxides containing about 0·3 per cent. of cobalt and 0·1 per cent. of nickel, besides copper and lead. This fissure is estimated to contain at least 30,000 kilos. of cobalt.

The author, in conclusion, suggests the recovery of cobalt from iron and copper pyrites.

D. B.

Strontianite and Celestine from the Kaiserstuhl. By J. BECKENKAMP (*Zeit. Kryst. Min.*, **14**, 67—73).—Strontianite, a mineral hitherto unknown in Baden, has been found by the author at Oberschaffhausen. On analysis it gave the following results:—

CaO.	SrO.	CO_2.	Mg.	Fe.	Total.
4·91	63·94	30·92	trace	trace	99·77

It occurs in prismatic crystals, and in crystals resembling tetrahedra, which are shown to be hemimorphic. At the same locality, the author found blue crystals of celestine. B. H. B.

Chemical Structure of Natural Silicates. By F. W. CLARKE (*Amer. Chem. J.*, **10**, 120—128).—From the relatively small number of silicates and the repeated occurrence of the same silicates under the most varied circumstances, it follows that their constitution must be comparatively simple. They may generally be regarded as substitution derivatives of ortho- or of meta-silicic acid, or of polymerides of the same acids. To these views the author was led by noticing the change of topaz into muscovite ($Al_2SiO_4F_2$ into $Al_3KH_2(SiO_4)_3$); these formulæ exhibit no distinct relationship until the former is trebled, and both are written as orthosilicates, $Al(SiO_4Al)_2{\cdot}SiO_4(AlF_2)_3$, and $Al(SiO_4Al)_2{\cdot}SiO_4KH_2$. The following minerals are cited as being orthosilicates, and constitutional formulæ are assigned to them: Xenolite, fibrolite, paragonite, eucryptite, dumortierite, grossularite, prehnite, and natrolite; the formulæ exhibit relationships that are confirmed by the mode of occurrence of the several minerals. The same holds good with the alteration products westantite, montmorillonite, and kaolinite, and with the polymerides annite, sodulite, nosean, and ultramarine.

The metasilicate of aluminium does not occur native; it might be written either $SiO_3(Al\vdots SiO_3)_2$, or $Al(SiO_3)_3Al$, but as far as can be judged from the native metasilicates, the former formula is the only one admissible. Spodumene, jadeite, leucite, pyrophyllite, kyanite, are regarded as belonging to this class; the latter being represented as $SiO_3\vdots Al{\cdot}O{\cdot}AlO$.

There are also a couple of other silicic acids, $H_2Si_2O_5$, from which petalite is derived, and $H_4Si_3O_8$, from which only albite and orthoclase are derived. Other acids may exist, but it does not appear necessary to assume their existence.

By these formulæ, relationships can be traced between minerals derived from the different acids as is shown in the case of muscovite, garnet, tourmaline, and orthoclase, and albite, the constituent of all granites. The silicates, other than those of aluminium, present few difficulties in the consideration of their structure. It is possible that silicates exist that are partly ortho- and partly meta-compounds. Similarly, all double salts may be considered, but with some, as the double haloïds, acetates, formates, &c., the case is not so clear

H. B.

Composition of Tourmaline. By R. B. RIGGS (*Amer. J. Sci.*, **35**, 35—51).—With the exception of the researches of Rammelsberg, very little has been done towards solving the question of the composition and constitution of the varieties of tourmaline. Rammelsberg's analyses were faulty in that the water and boric acid were not directly estimated. The direct estimation of water being possible, and a satisfactory method of determining boric acid having been devised by Gooch (Abstr, 1887, 299), new tourmaline analyses seemed desirable. The author has therefore analysed material from the following localities:—Auburn, Rumford, and Paris, in Maine; Calhao in Brazil; Dekalb, Gouverneur, and Pierrepoint in New York; Hamburg in New Jersey; Orford in New Hampshire; Monroe and Haddam in Connecticut; Stony Point in North Carolina; and Nantic Gulf in Baffin's Land. These represent well the variations in physical properties and chemical composition, which characterise the different varieties of tourmaline. From the analytical results, it is evident that there are three types, lithia, iron, and magnesia tourmaline respectively, with an indefinite number of intermediate products. These types graduate from one into the other, beginning with the lithia tourmaline, and passing through the iron varieties to those of the purer magnesian type.

The following formulæ may be taken as representing typical compounds of the three varieties:—

I. Lithia tourmaline—

$$12SiO_2,3B_2O_3,4H_2O,8Al_2O_3,2(NaLi)_2O.$$

II. Iron tourmaline—

$$12SiO_2,3B_2O_3,4H_2O,7Al_2O_3,4FeO,Na_2O.$$

III. Magnesia tourmaline—

$$12SiO_2,3B_2O_3,4H_2O,5Al_2O_3,\tfrac{28}{3}MgO,\tfrac{2}{3}Na_2O.$$

The calculated theoretical composition of these types is as follows:—

	B_2O_3.	SiO_2.	Al_2O_3.	FeO.	MgO.	Li_2O.	Na_2O.	H_2O.	Total.
I.	11·00	37·70	42·75	—	—	1·57	3·21	3·77	100·00
II.	10·18	34·89	34·59	13·95	—	—	2·90	3·49	100·00
III.	10·90	37·38	26·49	—	19·31	—	2·18	3·74	100·00

On comparing these results with those of analysis, they will be found to agree closely. The boric acid found invariably falls short of the theory. This is not to be wondered at, as the analyses are made of material more or less impure, and the case would be exceptional where the impurity tended to raise the percentage of boric acid. The author intends to discuss more fully the composition of tourmaline in a paper which is to appear in a forthcoming bulletin of the United States Geological Survey. B. H. B.

Genthite. By P. H. WALKER (*Amer. Chem. J.*, **10**, **44**).—A fresh analysis of a sample from Webster, Jackson Co., N.C., U.S. (Compare Dunnington, this Journal, 1872, 680). Hardness 2·5; sp. gr. 2·53.

SiO_2.	NiO.	MgO.	H_2O at 100°.	H_2O above 100°.	Fe_2O_3.	
55·38	17·84	15·62	5·18	5·59	0·56	= 100·17

H. B.

Nickeliferous Talc. By I. A. Bachman (*Amer. Chem. J.*, **10**, 45).—The specimen was from Webster, Jackson Co., N.C., U.S. It is notable for the large amount of nickel contained in it:—

SiO_2.	NiO.	MgO.	Fe_2O_3.	Al_2O_3.	H_2O at 100°.	H_2O above 100°.
53·91	15·91	19·39	1·46	2·65	0·80	5·50 = 99·62

H. B.

Tscheffkinite. By R. C. Price (*Amer. Chem. J.*, **10**, 38—39).—The specimen, a large, single block, lying loose on the ground, is from Hat Creek, Massie's Mills, Nelson Co., Va., U.S.

SiO_2.	TiO_2.	ZrO_2.	Ce_2O_3.	Di_2O_3.	La_2O_3.	Fe_2O_3.	FeO.	BeO.
23·28	21·16	2·29	11·89	15·38	4·96	5·63	5·56	2·15

CaO.	MgO.	Na_2O.	H_2O.
5·48	0·64	0·32	1·90 = 100·64

Previous published analyses and also the present one approximate to the formula $2(Ca,Be,Fe,Mg)O,(Ce,Di,La,Fe)_2O_3,5(Si,Ti)O_2$.

H. B.

Zobtenite. By J. Roth (*Chem. Centr.*, 1887, 1235, from *Preus. Akad. Wiss. Nat. M.*, 265—284).—Zobtenite is described as a petrographic rock belonging geologically to the crystalline schists, and corresponding to eruptive gabbro. The usual coarse-grained zobtenite is composed of saussuritic labradorite, grey or green diallage, some magnetic iron, and pyrites. The labradorite is mostly changed into an aggregate of zoisite and epidote with hornblende; the diallage into uralite. Serpentine and plagioclase-amphibolite occur in intimate association with the occasionally coarse-veined zobtenite. The same group of rocks is met with in the Baumgarten-Groschauer mountain, and the same interlacing of serpentine, hornblende schists, and zobtenite (veined gabbro) occurs also in Saxon granulite. This interlacing is seen very well at Rosswein, Böhrigen and Höllmuhle. Zobtenite here and there contains hypersthene and olivine. It is also found with chloritic schists and serpentine at Wagaleite in the Fichtelgebirge, and here is composed of saussuritic labradorite with coarse grossularite, diallage, and titanic iron. At Frankenstein, fine and coarse-grained zobtenite is found bearing hornblende, quartz, apatite, magnetite, iron pyrites, and more rarely rhombic pyroxene and secondary biotite. The widely distributed veined zobtenite found in the Jotunfjelds of Norway, is composed of plagioclase, sea-green diallage, hypersthene, green hornblende, apatite, magnetite, spinelle, and garnet, with transitions in the schists.

The bright coloured labradorite rock of Närödal is composed of labradorite, diallage, and garnet.. The hyperytes of Vermland (plagioclase, augite, hypersthene, olivine, apatite, and titanic iron) change into dioritic rocks, and are intimately mixed with the surrounding magnetite gneiss. The modifications contain labradorite, green diallage with uralite, hypersthene, and garnet. In Roslagen, transitions of pure diorite through dioritic diallage to gabbro are found. The latter contains anorthite, diallage, hornblende, magnetite, olivine, augite, hypersthene, enstatite, apatite, mica, quartz, pyrites, graphite, epidote, saussurite, and small quantities of zircon and picotite.

The gabbro of Radmansö is developed as gabbro, olivine-gabbro, and hornblende-gabbro, besides transitions occur as quartz, and biotite gabbro, and diallage gneiss. J. P. L.

Meteoric Iron from Nejed, Central Arabia. By L. Fletcher (*Min. Mag.*, 7, 179—183).—A meteoric iron, weighing 59·4 kilograms, was seen to fall in the district of Nejed, Central Arabia, on June 18th, 1863. The mass is tetrahedral in shape, its length being 41 cm., and its breadth and thickness both 28 cm. The surface is covered with pittings, and there is no evidence of weathering. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Insol. residue.	Total.	Sp. gr.
91·04	7·40	0·66	0·10	0·59	99·79	7·863

Traces of copper and sulphur were observed. The black residue insoluble in aqua regia, consists chiefly of amorphous carbon containing a trace of chromite. In composition, the Nejed iron is very similar to the Trenton, Toluca, and the Verkhne Udinsk irons.

B. H. B.

Meteoric Iron from Greenbrier Co., West Virginia. By L. Fletcher (*Min. Mag.*, 7, 183—186).—A single fragment of iron, weighing 11 lbs., was found in 1880 on the Alleghany Mountain, Greenbrier Co., West Virginia. Two pieces, weighing 63 and 31 oz. respectively, were acquired for the British Museum. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Residue.	Total.	Sp. gr.
91·59	7·11	0·60	0·08	0·12	99·50	7·869

The insoluble residue consisted of graphitic carbon, and a fine powder, small fragments, a thin elongated plate, and a single opaque black crystal with bright faces and a metallic lustre. These were found to be chromite. The existence of crystallised chromite in meteoric irons has hitherto not been completely established. The only instance appears to be recorded by Shepard in the iron of the Seneca River. The above percentage composition is approximately that of the Trenton, Rio Juncal, Seneca River, and Staunton irons.

B. H. B.

So-called Northport Meteorite. By F. C. Robinson (*Amer. J. Sci.*, 35, 212—213).—A specimen of a black stone described as a meteorite which fell in Northport, Maine, gave on analysis the following results:—

Fe.	Al.	Cu.	Mg.	Co.	SiO_2.	S.	P.	Total.
43·37	4·19	0·88	2·05	0·25	27·68	1·10	0·03	79·55

Traces of manganese were observed. The magnesium, aluminium, and most of the iron were evidently combined as silicates. The rest of the iron was present as sulphide and oxide, and the copper as sulphide. Sections under the microscope closely resemble those made from furnace slag. It will be noticed, too, that the analysis corresponds very closely with published analyses of slag. In fact the so-called meteorite is identical in composition with copper-slag from the old Revere Copper Works in Massachusetts. Although there can be no doubt that this specimenn is an old copper-slag, still the fall of a meteorite at Northport cannot be questioned, and true meteoric fragments may possibly yet be found there. B. H. B.

Organic Chemistry.

Fire-damp. By C. Winkler (*J. pr. Chem.* [2], **37**, 254—258).—This is a controversial paper, in which the author states that many of the opinions advanced by Franke (this vol., p. 570) are not in accordance with those held by experts. G. T. M.

Allylene. By A. Béhal (*Bull. Soc. Chim.*, **48**, 788—799).—A number of experiments, made with a view to prepare symmetrical allylene, are described. The compounds employed were allyl iodide, trimethylene bromide, allyl alcohol, α- and β-epidichlorhydrin, &c.

The experiments of Aarland (*J. pr. Chem.* [2], **6**, 256) on the electrolysis of itaconic acid were repeated, but only negative results were obtained, from which the author concludes (1) that allylene, $CH_2\colon C\colon CH_2$, has not yet been isolated; (2) that it is possible that the compound is not capable of existing. Further, it is pointed out that the reactions hitherto employed for preparing allylene—(Hartenstein acted on β-epichlorhydrin with sodium (*J. pr. Chem.* [2], **7**, 310)—ought to yield not this substance, but closed-chain compounds.

N. H. M.

Trichloralcohol: Action of Zinc Ethide on Aldehydes. By M. Delacre (*Bull. Soc. Chim.*, **48**, 784—788).—40 grams of zinc ethide are dissolved in about 700 c.c. of absolute ether and gradually treated with an ethereal solution of 51 grains of chloral. After 24 hours, crystals of the compound $ZnEtO\cdot CH_2\cdot CCl_3$ separate. If 48 grams of chloral is now added to the mixture, a further reaction takes place, and zinc trichlorethoxide, $Zn(O\cdot CH_2\cdot CCl_3)_2$, separates as an abundant, white, pulverulent precipitate.

Phosphorus trichloride acts on trichloralcohol with liberation of hydrogen chloride and formation of *trichlorethyl phosphite*. This is a clear liquid which fumes only slightly when freshly distilled.

Phosphorus pentachloride reacts with trichloralcohol, yielding the compound $CCl_3\cdot CH_2Cl$; to complete the reaction, the mixture is afterwards heated at 140°. The new compound has an aromatic odour, melts at 73—74°, and sublimes; it is very soluble in ether, sparingly soluble in light petroleum. N. H. M.

Constitution of Guthrie's Chlorethyl Bisulphide. By W. Spring and A. Lecrenier (*Bull. Soc. Chim.*, **48**, 629—630).—By the action of sulphur chloride on ethylene, Guthrie obtained (*Annalen*, **119**, 91, and **121**, 108) the two compounds $S_2(C_2H_4Cl)_2$ and $S_2(C_2H_3Cl_2)_2$. When the former compound is oxidised with nitric acid, β-chlorethylsulphonic acid is formed, the lead salt of which when heated with ammonia yielded taurine. The constitution of Guthrie's compound is therefore $S_2(CH_2\cdot CH_2Cl)_2$. N. H. M.

Cyanogen Compounds of Sulphines. By G. Patein (*Compt. rend.*, **106**, 861—863).—The author has prepared the iodides of the sulphines, SMe_3I, SEt_3I, $SMeEt_2I$, and SMe_2EtI, which will be described subsequently. The sulphur seems to play the same part as the nitrogen in ammonia.

If the hydriodide of triethylsulphine iodide is dissolved in alcohol at 90°, and mixed with silver cyanide, some heat is developed, and if the product is filtered and the filtrate evaporated in a vacuum, the compound $SEt_3Cy,AgCy$ is obtained in crystals. These are dissolved in alcohol and mixed with ether, when a syrupy liquid is precipitated which crystallises in a vacuum over sulphuric acid. The corresponding methyl compound is obtained in a similar manner and crystallises in long needles. The compounds $SMeEt_2Cy,AgCy$ and $SMe_2EtCy,AgCy$ were also prepared. They all crystallise well and are soluble in alcohol in almost all proportions, but are insoluble in ether. They melt readily without decomposition, but at 2° or 3° above the melting point the sulphine cyanide volatilises and silver cyanide is left. All except the trimethyl compound are deliquescent, and the attraction for water increases with the number of ethyl groups. They are partially decomposed by water with separation of silver cyanide. When treated with acids, half the cyanogen is evolved as hydrocyanic acid, and a salt of the sulphine is formed, silver cyanide being precipitated. With hydrochloric acid, the silver separates as silver chloride; if the compound is treated with silver nitrate, the whole of the cyanogen is removed in the form of silver cyanide. C. H. B.

Action of Chlorine on the Sulphides of Alcoholic Radicles. Preparation of some new Chlorine-derivatives. By W. Spring and A. Lecrenier (*Bull. Soc. Chim.*, **48**, 623—628).—When sulphur derivatives (sulphides, hydrosulphides, and bisulphides) of propyl, isobutyl, and amyl are treated with dry chlorine in diffused daylight, in presence of a little iodine, reactions take place with considerable development of heat, causing the liquids to boil. No chlorinated sulphides are formed, the sulphur being eliminated as dichloride; much hydrogen chloride is evolved.

In the case of propyl sulphide, the two chlorides $CEtCl_3$ and $C_3H_2Cl_6$ are obtained. The former compound, which had not been previously prepared, is a liquid boiling at 145—150°; its constitution was determined by heating it with silver oxide and water, when it yields silver chloride and propionate.

Isobutyl sulphide yielded the dichloride $C_4H_8Cl_2$, boiling at 105°, a new *trichloride*, $CPrCl_3$, and a crystalline tetrachloride, $C_4H_6Cl_4$. Amyl sulphide gave a mixture of six chlorides:—$C_5H_{11}Cl$, $C_4H_7\cdot CHCl_2$, $CHMe_2\cdot CH_2\cdot CCl_3$, $C_5H_8Cl_4$, a *pentachloride*, $CHMe_2\cdot CCl_2\cdot CCl_3$, and a *hexachloride*, probably $CMe_2Cl\cdot CCl_2\cdot CCl_3$. N. H. M.

Trimethylene: Formation of Allyl Alcohol from Symmetrical Dichlorhydrin. By H. Tornöe (*Ber.*, 21, 1282—1291).—Trimethylene was prepared by the action of zinc-dust on trimethylene bromide in presence of alcohol.

Allyl alcohol was obtained by the method of Hübner and Müller, by the action of sodium on symmetrical dichlorhydrin. The dichlorhydrin must always be in excess, and should be kept cold by means of ice and hydrochloric acid. The yield is about 50 per cent. of the theoretical. To free it from chlorine, it is heated at 70° with potash, when an oil of the formula $(C_{10}H_{18}O_4)_n$ is formed. This boils at 227—229°. Allylthiocarbamide melts at 78·4°, and is sparingly soluble in ether.

Allyl carbamate, $C_4H_7NO_2$, is prepared by passing carbonyl chloride through allyl alcohol and treating the fractionated product with ammonia. It is readily soluble, melts at 21·5—22° and boils at 203—204°. Preparations were made from ordinary allyl alcohol and from allyl alcohol prepared as given above.

When pure dichlorhydrin from epichlorhydrin is reduced with 5 per cent. sodium amalgam, a few drops of allyl alcohol is formed, the chief product being an oil which boils at 114°. When this is treated with dry hydrogen chloride, it is converted into symmetrical dichlorhydrin. The oil was therefore epichlorhydrin. When this is treated with sodium amalgam, the greater part remains unchanged; a few drops of allyl alcohol are formed but no isopropyl alcohol. (Compare Buff, *Annalen*, Suppl. 5, 242). N. H. M.

Oxidation of Olefines and of Alcohols of the Allyl Series. By G. Wagner (*Ber.*, 21, 1230—1240).—Olefines yield the corresponding glycols, and alcohols of the allyl alcohol series yield glycerols when oxidised with potassium permanganate in neutral, aqueous solution. The yield of glycol is about 50 per cent., that of the glycerol in some cases about 80 per cent., of the theoretical quantity.

Isobutylene yields the glycol, part of which is further oxidised to hydroxyisobutyric acid; the latter then decomposes into acetone and formic acid, part of the acetone being further oxidised to acetic acid. (Compare O. and F. Leidler, Abstr., 1879, 907.)

Isopropylethylene gives the corresponding glycol, which is partially converted into isobutylformic acid; the latter splits up into formic acid and isobutaldehyde, which is further converted into acetone and acetic acid. (Compare Leidler, this Jour., 1877, ii, 421.)

Ethylene yields the glycol and formic acid.

Trimethylethylene, prepared from the iodide of tertiary amyl alcohol, gives a mixture of trimethylethylene glycol and unsymmetrical methylethylene glycol, which shows that two olefines are produced by acting on the tertiary iodide with alcoholic potash.

Acetone, a few drops of a higher boiling compound, and acetaldehyde were also obtained.

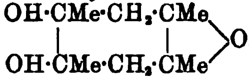
Isodibutylene yields small quantities of oxoctenol, and a glycol which boils at 216—218° and crystallises from light petroleum in shining, well-defined rhombohedrons melting at 59·5°.

Trimethylene is not oxidised by potassium permanganate, but diallyl yields a tetrahydroxy-alcohol, and pinene yields a dihydroxy-alcohol.

Allyl alcohol, ethylvinyl carbinol, allylisobutyl carbinol, methylallyl carbinol, and dimethylallyl carbinol, all give the corresponding glycerol. F. S. K.

Derivatives of Acetylacetone: Synthesis of Polyatomic Alcohols. By A. COMBES (*Bull. Soc. Chem.*, **48**, 474—483).—An aqueous solution of acetylacetone is treated with a little hydrochloric acid, and then with 1 per cent. sodium amalgam in small amounts, the liquid being always kept acid. After some days the whole is treated with a large excess of potassium carbonate, and extracted with chloroform. The extract contains two compounds, amylic glycol and the anhydride of a tetratomic alcohol, which are separated by fractional distillation.

Normal amylic glycol, $OH\cdot CHMe\cdot CH_2\cdot CHMe\cdot OH$, is a colourless liquid of a rather agreeable odour boiling at 177°. When cooled, it becomes syrupy; it is very soluble in water.

The *anhydride*, 

$$\begin{array}{l} OH\cdot CMe\cdot CH_2\cdot CMe \\ \quad\;\; | \qquad\qquad\quad | \\ OH\cdot CMe\cdot CH_2\cdot CMe \end{array} > O$$

is a yellowish liquid having an odour resembling that of glycol, and boils at about 270°.

When acetylacetone is heated with hydriodic acid (sp. gr. 1·8) at 180—185° for some hours, it is converted into normal pentane. If less concentrated hydriodic acid is used, and a temperature of 100—105°, the two iodides $CHMeI\cdot CH_2\cdot CH_2Me$ and $CH_2\cdot(CHMeI)_2$ are obtained.

Acetylacetone hexachloride, $CH_2(CO\cdot CCl_3)_2$, is prepared by saturating the cold ketone with chlorine; the product is heated in a retort exposed to sunlight, dry chlorine is passed through it for several days, and the dense liquid is washed with water. It is colourless, has a pungent odour, and is very irritating to the eyes; it boils at 190—200° under 20 mm. pressure. When treated with dilute aqueous soda, trichloracetone is formed. Ammonia acts on it with formation of much chloroform, together with some acetamide.

Acetylacetone hexabromide, $CH_2(CO\cdot CBr_3)_2$, obtained by treating acetylacetone with 13 times its weight of bromine, crystallises in colourless needles melting at 107—108°. It resembles the hexachloride in its behaviour towards alkalis.

When dry ammonia is passed through acetylacetone dissolved in ether, the compound $NH_4\cdot CH(COMe)_2$ separates in colourless spangles; it is very unstable, and decomposes into acetylacetone and ammonia when exposed to air; if heated in a closed tube at 25—30°, it yields a mixture of acetone and acetamide.

Amines react with acetylacetone with formation of nitrogenous compounds. N. H. M.

Levulose. By A. HERZFELD (*Annalen*, **244**, 274—295).—Most of the contents of this paper have already appeared (Abstr., 1886, 438, 862). The author confirms Scheibler's statement (Abstr., 1884, 574) that the reduction of levulose to mannitol by sodium amalgam is, in the first instance, due to the action of the sodium hydroxide on the levulose, and, secondly, to the action of the nascent hydrogen on the decomposition products. Levulose is not reduced by nascent hydrogen in acid solutions. W. C. W.

Isodulcitol. By B. RAYMAN and J. KRUIS (*Chem. Centr.*, 1888, 6, from *Listy. Chem.*, **12**, 7—11).—The striking similarity of quercite to glucose led the authors to determine whether the sugar obtained from the bark of the yellow oak did not actually contain glucose. The phenylhydrazine hydrochloride reaction showed the presence of a glucose in all portions of the sugar. Its reactions with hydrochloric acid very much resemble those of arabinose, the methyl ether of which it might be. When heated with hydriodic acid at 120°, however, no methyl iodide is formed. As it is shown that the reactions described by Raymann (Abstr., 1887, 906) are themselves applicable to isodulcitol, and as the analogy of the sugar $C_6H_{12}O_5$ to the dextrose series is brought into prominence, the authors propose to call it *rhamnose*, because it also appears to be identical with the sugar obtained by Liebermann from Rhamnus, the term isodulcitol being retained exclusively for the hexatomic alcohols. With solutions containing 15 to 30 grams, the rotatory power of rhamnose remains unchanged, $[\alpha]_D = +9\cdot3$; fresh solutions are more active, $[\alpha]_D = +12\cdot3$ to $+13$. In alcoholic solution, the specific rotatory power decreases as the relation of alcohol to sugar increases, until a point is reached at which the rotatory power is *nil;* from this point it becomes lævorotatory. The authors explain this phenomenon by assuming that rhamnose contains a carbonyl-group which is combined with water, so that the sugar $C_6H_{12}O_5,H_2O$ contains the group $\colon C(OH)_2$, which in watery solution remains unchanged, and is symmetrical. In alcoholic solution, however, the attraction of the carbonyl for water is destroyed, and the alcohol reacts with the carbonyl forming the group $\colon C(OH)\cdot OEt$, which is asymmetric. This group they consider causes the lævorotatory action. This supposition has some support, the authors consider, from the fact that rhamnose when dehydrated by boiling with absolute alcohol increases in weight to the extent of $\frac{1}{8}$.
J. P. L.

Molecular Weight of Raffinose. By H. DE VRIES (*Compt. rend.*, **106**, 751—754).—The author has determined the isotonic coefficient of raffinose by the method previously described (Abstr., 1884, 1065), using the middle ribs of the leaves of *Tradescantia discolor*. A solution containing 5·957 per cent. of raffinose is isotonic with a solution of saccharose containing 0·1 gram-molecule per litre. It follows that the molecular weight of raffinose is about 595·7, and this result agrees with the molecular weight of 594, corresponding with the formula $C_{18}H_{32}O_{16} + 5H_2O$ adopted by Loiseau and by Scheibler.
C. H. B.

Inactose of Neutral Sugar. By E. J. MAUMENÉ (*Bull. Soc. Chim.*, **48**, 773—777).—40 grams of a mixture of equal parts of sugar and of freshly-fused silver nitrate (free from acid) is dissolved in 100 c.c. of water; after 24 hours, the solution acquires a dark brown colour, which increases a little when the solution is heated on a water-bath. The product is filtered, and evaporated on a water-bath, when a colourless substance is obtained resembling the hydrate of phosphoric acid. When heated above 140°, it becomes gradually turbid, and water is given off. The filtered liquid has no rotatory power. The name *inactose* is ascribed to the new sugar. To obtain it free from silver, it is treated with a little calcium chloride, and filtered; alcohol is then added to the solution, which on evaporation under a glass cover deposits the sugar; this is washed with a little alcohol, redissolved, and the solution again evaporated as before. It forms a syrup, and could not be obtained in crystals. It unites with lime, but the compound produced is decomposed by carbonic anhydride, and the sugar so recovered is inactive as before. When a mixture of equal weights of sugar and silver nitrate is heated at 150—155° from two to three hours, a rather large amount of hexenenic acid is formed. N. H. M.

Iodide of Starch. By H. B. STOCKS (*Chem. News*, **57**, 183).—Moist iodide of starch was employed in the previous experiments (this vol., p. 126). Dry iodide of starch, prepared by adding iodine solution to starch-paste in water, precipitating with alcohol, filtering, and drying, is a black, lustrous substance, which is not decomposed by sunlight nor by heating at 100°, but at somewhat higher temperatures gives off tarry matter and iodine. It does not dissolve in water, and is decomposed by it only after prolonged boiling. Further experiments show that when free iodine acts on silver salts, some silver iodate is formed, and, moreover, tend to confirm the statement that the formation of iodide of starch is due to free iodine (*loc. cit.*). The author finds that the colour of iodide of starch varies with the proportion of iodine employed, but does not vary with different starches. Small quantities of iodine give an indigo-blue colour, larger quantities violet, whilst with an excess of iodine, the colour appears green, although the precipitated iodide is blue.

The colour is destroyed by permanganate, which attacks the starch; by iron filings, and by heating with alcohol, ethyl iodide being formed. Bromine destroys it by the formation of iodine bromide, the latter can be decomposed by carefully neutralising with sodium carbonate, and then the liberated iodine regenerates the blue colour. The iodide is precipitated, but not destroyed, by potassium dichromate. Zinc and sulphuric acid do not act on the colour. D. A. L.

Vinylamine. By S. GABRIEL (*Ber.*, **21**, 1049—1057).—*Vinylamine picrate*, $CH_2{:}CH{\cdot}NH_2,C_6H_3N_3O_7$, is formed when the reaction product of moist silver oxide and an aqueous solution of bromethylamine hydrobromide is distilled with steam, the distillate saturated with hydrochloric acid, and a solution of picric acid added. On standing, yellow needles, or short, compact forms separate. It crystallises from water in fine needles, which, after previously softening, melt at 142° to a reddish-yellow, blistered, glassy mass. When distilled with water, it yields an aqueous solution of vinylamine. *Vinylamine platinochloride*, $(C_2H_5N)_2,H_2PtCl_6$, crystallises in small, well-defined forms, which are readily soluble in water, but only very sparingly or not at all in alcohol. In an aqueous solution of this salt, Nessler's solution gives a yellowish-white precipitate. *Vinylamine bismutho-iodide*, $(C_2H_5NHI)_3,2BiI_3$, crystallises in shining, fiery-red, microscopic, regular, hexagonal leaves, which are almost insoluble in water and dilute acids. *Vinylamine aurochloride* forms flat, golden-yellow needles or plates. The readiness with which solutions of vinylamine platinochloride and aurochloride decompose is not due to the presence of the metallic chloride. An aqueous solution of the hydrochloride is completely decomposed on heating; an aqueous solution of the free base decomposes in the cold.

When an aqueous solution of vinylamine is neutralised with hydrochloric acid and evaporated at 50° or in a vacuum, a colourless syrup is obtained which contains the hydrochloride of a new base. This base yields a picrate which appears to be identical with β-hydroxyethylamine picrate (this vol., p. 440) and also with the picrates of the bases obtained by the action of potash on chlorethylamine and bromethylamine hydrochloride.

β-Chlorethylamine hydrochloride is obtained by evaporating a solution of vinylamine with a large excess of hydrochloric acid; β-bromethylamine hydrobromide is produced in a similar manner.

β-Iodethylamine hydriodide, $CH_2I\cdot CH_2\cdot NH_2,HI$, crystallises from hot, absolute alcohol in colourless, rhombic forms, which, after previously softening, melt and turn brown at 192—194°. It is readily soluble in water, and when treated with potash yields a disagreeably smelling oil which is soluble in water.

The *picrate*, $C_2H_6IN,C_6H_3N_3O_7,\frac{1}{2}H_2O$, crystallises in short, compact, yellow prisms, which, after previously softening, melt at about 105°. On heating slowly, they lose water of crystallisation, and then melt at 129—131°.

By evaporating a solution of vinylamine with excess of sulphuric acid, a syrup is obtained which crystallises from water in transparent rhombohedra having the composition $C_2H_7NSO_4$. This compound is readily soluble in warm water, softens above 230°, turns brown, and melts when heated on platinum foil, giving out an empyreumatic odour; on igniting, a carbonaceous residue is obtained.

F. S. K.

Action of Zinc-dust on Chloral. By K. Chodounsky (*Chem. Centr.*, 1888, 74, from *Listy. Chem.*, **12**, 57—59).—Chloral was allowed to fall drop by drop on to zinc-dust in a retort heated on an oil-bath and attached to a cooled receiver. At 100° the reaction is feeble, but above 120° it becomes very violent, so violent that part of the carbon separated in the reaction is carried over into the receiver. Carbonic oxide was formed, but no chloroform. Chloral was also heated with zinc-dust and zinc oxide in sealed tubes previously filled with carbonic anhydride. In the tubes containing zinc-dust heated at 120°, carbonic oxide, hydrogen, chloroform, and a product of lower boiling point (probably a lower chlorinated methane), besides carbon and zinc chloride, were found. In the zinc oxide tube, under the same conditions, much gas, zinc chloride, and the zinc salt of an organic acid were found, but no chloroform. In tubes containing zinc-dust and chloral heated at 160°, carbonic oxide, hydrogen, and acetylene were formed, and the liquid consisted of unchanged chloral and traces of chloroform.

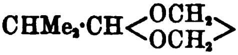
Zinc formate when heated in a retort gave carbonic oxide, hydrogen, carbonic anhydride, zinc oxide, and a little zinc. It appears that chloral is converted by zinc-dust partly into chloroform and zinc formate, and the latter into carbonic anhydride, carbonic oxide, and hydrogen. Chloroform also suffers partial decomposition, which increases with the temperature. J. P. L.

Action of Chloral Hydrate and Iodoform on Mercuric Salts. By S. Cotton (*J. Pharm.* [5], **16**, 481—483).—Chloral hydrate reduces mercuric acetate with evolution of carbonic anhydride and formation of mercurous acetate, whilst the same reagent with mercuric nitrate forms carbonic anhydride and mercurous chloride. Iodoform reduces mercuric acetate with evolution of carbonic anhydride and formation of mercurous acetate precisely in the same manner as chloral hydrate does, but iodoform does not reduce mercuric nitrate, its action being limited to the formation of the corresponding iodide. Chloroform and bromoform act on neither of these two salts. J. T.

Compounds of Glycol with some Aldehydes. By H. Lochert (*Bull. Soc. Chim.*, **48**, 337—338, and 716—718).—*Ethylene œnanthylidene oxide*, $C_6H_{13}\cdot CH<\begin{matrix}OCH_2\\OCH_2\end{matrix}>$, is prepared (1) by heating œnanthaldehyde (1 vol.) and glycol (3 vols.) for eight days at 125—130°, the upper layer of the product being then fractionally distilled; (2) by heating as in (1) a mixture of œnanthaldehyde (1 vol.), glycol (2 vols.), and glacial acetic acid (1 vol.). The mixing of the glycol and *a*-aldehyde gives rise to considerable development of heat. It is a mobile liquid, boiling at about 180°, and having an odour resembling that of œnanthaldehyde but less pronounced.

From glycol and valeraldehyde the compound $C_4H_9\cdot CH<\begin{matrix}OCH_2\\OCH_2\end{matrix}>$ was obtained. This boils at about 142°, and has an agreeable ethereal odour.

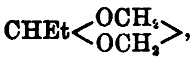
When a mixture of glycol (2 mols.) and isobutaldehyde (1 mol.) is heated in a water-bath for seven days, the compound



$$CHMe_2\cdot CH<\begin{matrix}OCH_2\\OCH_2\end{matrix}>$$

is obtained. It is a colourless, refractive liquid, boiling at 124—126°, soluble in 10 parts of water, very soluble in alcohol and ether. When heated in a closed tube at 140° for two days, it is decomposed into its original constituents. Caustic potash and dry alkalis have no action on it.

Propaldehyde and glycol yield the condensation product



$$\mathrm{CHEt}<\begin{matrix}\mathrm{OCH_2}\\ \mathrm{OCH_2}\end{matrix}>,$$

a colourless liquid having an odour resembling that of propaldehyde and boiling at 105—107°. N. H. M.

Action of Bromine on the Compounds of Glycol with Aldehyde. By H. Lochert (*Bull. Soc. Chim.*, **48**, 718—719).—Bromine reacts with the compounds of aldehydes with glycol (preceding Abstract), yielding monobromo-derivatives.

Acetoacetaldehyde. By L. Claisen and N. Stylos (*Ber.*, **21**, 1144—1149).—The *sodium* compound of acetoacetaldehyde,

$$\mathrm{CHNaAc{\cdot}COH},$$

is obtained by adding a mixture of acetone (1 mol.) and ethyl formate (1 mol.) to sodium ethoxide (1 mol.) free from alcohol and suspended in anhydrous ether cooled in ice. It is very soluble in water, gives a dark yellowish-red coloration with ferric chloride, and on treatment with copper acetate yields the *copper* salt $(C_4H_5O_2)_2Cu$, which crystallises in bright blue needles, and is soluble in hot benzene and ether. The *anilide*, *toluidide*, and *naphthalide* were also prepared. The *benzene-azo*-derivative, $COH{\cdot}CHAc{\cdot}N_2Ph$, is crystalline, and melts at 117—118°. Addition of phenylhydrazine to the concentrated aqueous solution of the sodium salt free from acetone converts it into a *methylphenylpyrazole* (? Ph : Me = 1 : 5), which has a sp. gr. = 1·081 at 15°, boils at 254—257°, and is probably identical with that obtained from ethyl acetopyruvate (this vol., p. 676). It is, however, solid at the ordinary temperature, and melts at 36—37°. Acetoacetaldehyde could not be isolated owing to its tendency to undergo condensation with the formation of symmetrical triacetylbenzene.

1 : 3 : 5 *Triacetylbenzene*, $C_6H_3Ac_3$, is obtained by treating the above product with a small quantity of ice-cold water, separating the upper ethereal layer, and treating the lower aqueous layer with an equivalent quantity of acetic acid. It crystallises in small, white needles, melts at 162—163°, is readily soluble in acetic acid, sparingly soluble in alcohol, ether, and water, and on oxidation with concentrated nitric acid is converted into trimesic acid.

The following compounds were prepared by Meyerwitz:—*Sodium propionylacetaldehyde*, $COEt{\cdot}CHNa{\cdot}COH$, and the corresponding *ethyl phenylpyrazole*, $C_{11}H_{12}N_2$, a colourless liquid boiling at 273—275°, and having a sp. gr. = 1·064 at 15°; *sodium butyrylacetaldehyde*,

$$\mathrm{COPr{\cdot}CHNa{\cdot}COH},$$

its *copper* salt crystallising in flat, greenish prisms, and the corresponding *pyrazole*, $C_{12}H_{14}N_2$, a colourless oil boiling at 279—281° and having a sp. gr. = 1·0435 at 15° ; *sodium heptoylacetaldehyde*,

$$\mathrm{C_6H_{13}{\cdot}CO{\cdot}CHNa{\cdot}COH},$$

and the corresponding *pyrazole*, $C_{18}H_{20}N_2$, a thick oil boiling at 318—320°. W. P. W.

Action of Carbonyl Chloride on Sodium Formate. By R. Otto (*Ber.*, **21**, 1267—1268).—Hentschel (Abstr., 1884, 991) prepared acid anhydrides by the action of carbonyl chloride on the sodium salts of acetic and other acids. The author attempted to prepare formic anhydride by this method, but obtained only sodium chloride, carbonic anhydride, carbon monoxide, and formic acid. It is probable that formic anhydride is not capable of existing. N. H. M.

Chloro-derivatives of Ethyl Acetate. By M. Delacre (*Bull. Soc. Chim.*, **48**, 706—716; compare Abstr., 1887, 713).—*Chlorethyl dichloracetate*, $CHCl_2·COO·C_2H_4Cl$, is prepared by mixing chloracetic chloride with glycol chlorhydrin in molecular proportion, keeping the whole cool; the mixture is afterwards heated on a water-bath until no more hydrogen chloride is evolved, and precipitated with water; it is then made alkaline, separated, and dried with calcium chloride. It boils at 209—212° under 767 mm. pressure, and has an agreeable, aromatic odour; sp. gr. = 1·200 at 15°.

Chlorethyl trichloracetate, $CCl_3·COO·C_2H_4Cl$, is obtained from trichloracetic chloride in a manner similar to the dichloracetate. It has an agreeable, aromatic odour, and boils at 217° under 766 mm. pressure; sp. gr. = 1·251 at 15°.

Dichlorethyl monochloracetate, $CH_2Cl·COO·C_2H_3Cl_2$, prepared by distilling a mixture of dichlorethyl alcohol and chloracetic chloride, boils at 215° (corr.) under 760 mm. pressure; sp. gr. = 1·216 at 15°.

Dichlorethyl dichloracetate, $CHCl_2·COO·C_2H_3Cl_2$, boils at 223° under 756 mm. pressure; sp. gr. = 1·25 at 15°.

Dichlorethyl trichloracetate, $CCl_3·COO·C_2H_3Cl_2$, boils at 230° under 760 mm. pressure; it could not be solidified.

Trichlorethyl acetate (Thurnlackh, Abstr., 1882, 295) boils at 170° (corr.) under 747 mm. pressure; sp. gr. = 1·189 at 15°.

Trichlorethyl chloracetate, $CH_2Cl·COO·C_2H_2Cl_3$, is obtained by heating for some time and then distilling a mixture of acetic chloride and trichlorethyl alcohol. It boils at 220° (corr.) under 767 mm. pressure. When freshly distilled, it has a slightly acid odour, which changes to a feebly aromatic odour; sp. gr. = 1·25 at 15°.

Trichlorethyl dichloracetate, $CHCl_2·COO·C_2H_2Cl_3$, boils with slight decomposition at 230—231° under 767 mm. pressure; sp. gr. 1·267 at 15°. When kept, it decomposes with evolution of hydrogen chloride.

Trichlorethyl trichloracetate, $CCl_3·COO·C_2H_2Cl_3$, boils at 236° under 767 mm. pressure with slight liberation of hydrogen chloride. It is crystalline, and melts at 24—26°; when kept, it melts at the ordinary temperature, a little hydrogen chloride being given off.

When acetic chloride and acetaldehyde are mixed, the temperature of the mixture rises to 60° or 80°; with paraldehyde, cold is first produced, and then a development of heat takes place in consequence of the reaction between the acetic chloride and depolymerised aldehyde.

Acetic chloride reacts with anhydrous dichloraldehyde with formation of the compound $CH_3·COO·CHCl·CHCl_2$. This boils at 185°, has a fruity odour, and gives off hydrogen chloride when kept. With acetic chloride (2 mols.) and the hydrate of dichloraldehyde the compound $CHCl_2{\cdot}CH(OAc)_2$ is obtained; this melts at 52° and boils at 220—222°.

When chloracetic chloride and dichloraldehyde (22 grams of each) are heated at 150° for 18 hours, the compound $CCl_3{\cdot}COO{\cdot}CHCl{\cdot}CHCl_2$ is formed. It is a colourless liquid of aromatic odour, boiling at 226—228° under 756 mm. pressure. N. H. M.

Volatile Acids of Suint. By A. BUISINE (*Bull. Soc. Chim.*, **48**, 639—642).—The acids present in suint do not pre-exist in the perspiration, but are formed under the influence of microbes; the maximum amount of acids is found after 8 to 10 days' fermentation. In order to obtain the acids, the liquid is evaporated to dryness, the residue extracted with alcohol, and the alcoholic solution evaporated; the residue is dissolved in water, acidified with phosphoric acid, steam distilled, and the amount of acid determined by titration. The separation and determination of the amounts of the various acids are effected by converting the mixed acids into ethyl salts and fractionally distilling. The following numbers show the relative amounts:—Acetic acid (60); propionic acid (25); butyric acid (5); valeric acid (4); caproic acid (3); and benzoic acid (3). Formic and caprylic acids and phenol are present only in traces.

The amount of propionic acid in 1 cub. metre of suint water is about 5 or 6 kilos. (compare *Bull. Soc. Chim.*, **46**, 479).

N. H. M.

Millet Oil and some of its Products of Decomposition. By G. KASSNER (*Arch. Pharm.* [3], **25**, 1081—1101).—The oil of millet was treated with lead oxide, the product freed from water, and treated with ether. The solution after being filtered was shaken with sulphuric acid, separated, and evaporated. The oil is then kept in a closed vessel over pyrogallol and potash as it absorbs oxygen. Analyses of the acid and salts pointed to the formula $C_{18}H_{32}O_3$. It is probable that this hydroxy-acid is a product of oxidation of an acid, $C_{18}H_{32}O_2$, existing in millet.

When the oil of millet is oxidised with potassium permanganate, the acid $C_6H_{12}O_2$, probably *isobutylacetic acid*, and two acids, $C_6H_{11}O_2{\cdot}OH$ and $C_{14}H_{26}O_2(OH)_2$, are formed. The former hydroxy-acid crystallises in plates melting at 107—108°, readily soluble in water, and yields an *acetyl-derivative*, which melts at 70—71°. The acid, $C_{14}H_{26}O_2(OH)_2$, melts at 60°, is insoluble in water, readily soluble in alcohol and ether. The *alkali salts* are readily soluble, and could not be obtained in crystals.

When millet oil is fused with potash, acetic, lauric, and in small quantity butyric and oxalic acids are formed. When distilled, it yields an *acid*, $C_9H_{16}O_2$ or $C_{10}H_{18}O_2$, which boils at 216—220°.

The following partially-developed constitutional formulæ are suggested for the hydroxy-acid and the millet-oleic acid, from which it is supposed to be derived:—

$$C_6H_{12}O{:}CH{\cdot}CH{:}CH{\cdot}[CH_2]_{10}{\cdot}COOH \text{ and}$$

$$C_6H_{12}{:}CH{\cdot}CH{:}CH{\cdot}[CH_2]_{10}{\cdot}COOH.$$

N. H. M.

Oil from the Seeds of Curcas Purganus (formerly Jatropha Curcas). By F. M. Horn (*Zeit. anal. Chem.*, **27**, 163—165).—This oil, formerly employed as a purgative under the names *Oleum ricini majoris*, *Oleum infernale*, is at the present time much used for burning and for soap making, also for adulterating olive oil, and seemingly for making Turkey-red oil. It begins to crystallise at 9°, and is completely solid at 0°. At 15° its sp. gr. is 0·9192. It differs from castor oil in its very sparing solubility in alcohol. It appears to saponify readily in the cold, but in reality forms only acid soaps; for complete saponification heat is required, and solid potash acts better than solution.

It gives for Hehner's number, 87·9; for Reichert's, 0·65; for Köttstorfer's, 230·5; and for Hübl's, 127. M. J. S.

Constitution of Ethyl Sodacetoacetate and Ethyl Sodacetomalonate. By A. Michael (*Amer. Chem. J.*, **10**, 158—160).—Ethyl acetylmalonate has been prepared by Ehrlich, Conrad, and Guthzeit, from ethyl sodacetoacetate and ethyl chlorocarbonate, and lately by Lange from acetic chloride and ethyl sodiomalonate. But the acetates prepared by these two methods are not identical; the one being insoluble in strong cold alkaline solutions, the other being very readily soluble in any alkali, and boiling also 5° lower; moreover, in the latter process, ethyl diacetylmalonate is formed at the same time.

From these data it is concluded that whilst ethyl acetoacetate is correctly represented by the formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOEt$, the corresponding sodium compound is $CH_3{\cdot}C(ONa){:}CH{\cdot}COOEt$, and the substance obtained from it by the action of ethyl chlorocarbonate is $CH_3{\cdot}C(O{\cdot}COOEt){:}CH{\cdot}COOEt$. This certainly explains why the substance has no distinct acid properties like the real ethyl acetylmalonate, $CH_3{\cdot}CO{\cdot}CH(COOEt)_2$.

Further, Conrad and Guthzeit have prepared ethyl methenyltricarboxylate by the action of ethyl chlorocarbonate on ethyl sodiomalonate, and ascribe to it the constitution $CH(COOEt)_3$, and yet it is at once decomposed by alkalis and has no acid properties. The ethyl sodiomalonate used by these authors was first prepared in the solid state; but if ethyl chlorocarbonate is at once added to the product of the action of sodium on ethyl malonate, then a substance is obtained which has acid properties, forms a very stable sodium salt, and is doubtless expressed by the above formula, whilst the compound of Conrad and Guthzeit is $OEt{\cdot}C(O{\cdot}COOEt){:}CH{\cdot}COOEt$. This and the above constitutional formula for ethyl sodacetoacetate is explained on the assumption that sodium acting on ethyl malonate or ethyl acetoacetate forms at first sodium salts expressed by the usual formulæ, $COOEt{\cdot}CHNa{\cdot}CO{\cdot}OEt$ and $CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOEt$, but that owing to the affinity of sodium for oxygen, these are converted by heat, &c., into $OEt{\cdot}C(ONa){:}CH{\cdot}COOEt$ and

$$CH_3{\cdot}C(ONa){:}CH{\cdot}COOEt.$$

The action of sodium on isatin is probably similar. H. B.

Acetoacetic Acid and Ethyl Succinosuccinate. By A. HANTZSCH and F. HERRMANN (*Ber.*, **21**, 1084—1085).—A reply to the article by Geuther (this vol., p. 579).

Condensation Products of Urethane and Ethyl Acetoacetate. By J. MEISTER (*Annalen*, **244**, 233—253).—A condensation product of the composition $C_9H_{15}NO_4$ is prepared by heating at 140° in sealed tubes a mixture of urethane (10 grams), ethyl acetoacetate (20 grams), ether (10 grams), and a small quantity of ammonium chloride. It is easily decomposed by acids: thus with strong hydrochloric acid it yields ammonia, acetone, ethyl chloride, and carbonic anhydride.

As this substance is also formed by the action of ethyl chlorocarbonate on ethyl paramidoacetoacetate, it may be regarded as ethyl β-amidocrotonate, in which an atom of hydrogen is displaced by the group COOEt. Its constitution is represented by the formula COOEt·NH·CMe:CH·COOEt. It is not attacked by aqueous solutions of the alkalis, but is saponified by alcoholic potash, yielding an oily liquid of the composition $C_{12}H_{23}NO_6$.

A tribromo-derivative, soluble in alcohol and in ether, is obtained by the action of bromine on the condensation product suspended in water, but a corresponding trichloro-derivative could not be obtained.

At 160°, alcoholic ammonia acts on the condensation product, and crystals of the composition of β-uramidocrotonamide, containing 1 mol. of alcohol, are deposited. The crystals melt at 131°, and are soluble in hot alcohol. The same compound is formed by the action of alcoholic ammonia on ethyl β-uramidocrotonate. A corresponding anilide could not be prepared. The amide is decomposed by water, yielding urea, ammonia, acetone, alcohol, and carbonic anhydride. A strong boiling aqueous solution of potassium hydroxide decomposes the amide, yielding an oily liquid of the composition $C_{11}H_{20}N_2O_4$.

W. C. W.

Antimony Potassium Oxalate. By P. KAY (*Chem. News*, **57**, 193—194).—Two samples of this substance were found to correspond respectively with the formulæ $K_4Sb_2(C_2O_4)_5 + 3H_2O$ and $K_3Sb(C_2O_4)_3 + 2H_2O$. The antimony was estimated either by mixing the solution with tartaric acid, neutralising with sodium carbonate, adding potassium carbonate, then bleaching powder, and titrating the excess of the latter with sodium arsenite; or by direct titration with potassium hydroxide, using phenolphthaleïn as indicator. The potassium was estimated by converting into carbonate and titrating. The oxalic acid was determined in the usual way. D. A. L.

Derivatives of Ethylmalonic Acid. By M. FREUND and B. B. GOLDSMITH (*Ber.*, **21**, 1245—1247).—*Ethylmalonamide*,

$$CHEt(CONH_2)_2,$$

is obtained by acting on diethyl ethylmalonate with concentrated ammonia. It crystallises from alcohol, and melts at 207—208°.

Ethylmalonanilide, CHEt(CONHPh)$_2$, produced by heating diethyl ethylmalonate or ethylmalonamide with aniline, crystallises from alcohol in needles melting at 213—215°. It is insoluble in water, but dissolves readily in alcohol and glacial acetic acid.

Phenylethylmalonamide, $NH_2·CO·CHEt·CO·NHPh$, obtained by heating 1 mol. of the amide with 1 mol. of aniline, crystallises from water or alcohol, and melts at 182°.

Ethylmalonanilic acid, $COOH·CHEt·CO·NHPh$, is obtained by boiling the preceding compound with an excess of lime. It is soluble in alcohol, crystallises from water, and melts at 150° with evolution of carbonic anhydride. F. S. K.

Action of Ethyl Oxalate on Acetone. By L. Claisen and N. Stylos (*Ber.*, **21**, 1141—1143; compare Abstr., 1887, 917).—A very characteristic bluish-violet colour is formed when ethyl acetopyruvate is boiled with acetic acid and some sodium acetate. *Copper acetopyruvate*, $(C_{17}H_9O_4)_2Cu$, crystallises in small, bright-green needles. When the ethyl salt is boiled with phenylhydrazine in acetic acid solution, and the product treated with water, a thick oil is obtained which, after saponification with alcoholic soda, yields a white crystalline precipitate of a *methylphenylpyrazolecarboxylic acid*, $C_{10}H_9N_2·COOH$, on treatment with hydrochloric acid. The acid melts at 96°, but seems to contain either water or alcohol of crystallisation, since the melting point gradually rises to 134—136° by prolonged drying at 80—90°. At 200—210°, the acid loses carbonic anhydride, and is converted into a methylphenylpyrazole probably identical with that prepared from acetoacetaldehyde (this vol., p. 671), and isomeric with that obtained by Knorr (*Annalen*, **238**, 202); it has a sp. gr. = 1·085 at 15°, solidifies in a freezing mixture, and boils at 256—257° without decomposition.

Oxalyldiacetone, $CH_2Ac·CO·CO·CH_2Ac$, is obtained by adding to a well-cooled mixture of anhydrous ether and sodium ethoxide (2 mols.) free from alcohol, first acetone (2 mols.), and then ethyl oxalate (1 mol.), and allowing the product to remain for two days; the resulting yellow salt is then dissolved in water, and decomposed by the addition of acetic acid. It crystallises in white prisms, melts at 120—121°, is soluble in alcohol, ether, and chloroform, sparingly soluble in light petroleum and cold water, and gives a dark brownish-red coloration with alcoholic ferric chloride. W. P. W.

Derivatives of Saccharic and Mucic Acids. By Maquenne (*Bull. Soc. Chim.*, **48**, 719—723).—*Tetracetylmucic acid*,

$$C_4H_4(OAc)_4(COOH)_2 + 2H_2O,$$

is obtained by boiling mucic acid with acetic anhydride (2 parts) in presence of zinc chloride, until it is dissolved. The product is precipitated with water, washed, and crystallised from alcohol. It forms colourless, efflorescent needles, melting at 266° (corr.), sparingly soluble in water, readily soluble in hot alcohol; its reaction is strongly acid, but it does not form salts.

The lactone of diacetylsaccharic acid, $C_{10}H_{10}O_8$, is prepared by adding strong sulphuric acid, drop by drop, to a mixture of hydrogen potassium saccharate and acetic anhydride (2 parts). The product is precipitated by water and washed until no longer acid. It melts at 188° (corr.) without decomposition, and is sparingly soluble. It seems to be identical with the compound prepared by Baltzer by the action of acetic chloride on saccharic acid (*Annalen*, **149**, 241).

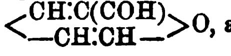
Saccharic acid diphenylhydrazide, $C_{18}H_{22}N_4O_6$ (Kiliani, this vol., p. 46) is obtained by heating an aqueous solution of saccharic acid, phenylhydrazine hydrochloride (each 8 grams), and sodium acetate (12 grams), on a water-bath for two hours. It is slightly yellow, melts at 210° with evolution of gas, is insoluble in water, alcohol, and ether, soluble in hot alcoholic potash. The diphenylhydrazide of mucic acid (Bülow, Abstr., 1887, 138) was prepared in a similar manner.

N. H. M.

Synthesis of Aspartic Acid. By A. Piutti (*Chem. Centr.*, 1888, 68—69, from *Rendi. Acc. Linc.* [4], **3**, 300—303).—Ethyl sodoxalacetate was prepared by treating 25 grams of ethyl oxalate and 15 grams of ethyl acetate dissolved in four times their weight of absolute ether, with 4 grams of sodium in small pieces. From this compound, the oxime was prepared by dissolving molecular proportions of the above compound and hydroxylamine hydrochloride in water, and gently warming. If the oily oxime which separates after a time is dissolved in ether, and the ether evaporated, a colourless oil is left, which soon appears blue or green by reflected, and violet by transmitted light. If a watery solution of this oxime is reduced with sodium amalgam, aspartic acid is formed.

The aspartic acid agrees in its properties with Dessaigne's acid and Piutti's inactive acid. The reduction of the oxime in watery, alcoholic and acetic acid solutions gives rise to highly coloured products, and small quantities of mono- and di-ethyl aspartates. Reduction of a watery solution of the oxime with ammonia also gives a good yield of acid.

J. P. L.

Furfuran-derivatives. By W. Marckwald (*Ber.*, **21**, 1398—1404).—The ethyl salt of the bibasic acid, $C_5H_8O(COOEt)_2$, obtained by treating furfuracrylic acid in alcoholic solution with hydrogen chloride (this vol., p. 135), and now termed *ethyl propiononedicarboxylate*, forms an *oxime*, $OH\cdot N{:}C_5H_8(COOEt)_2$, which crystallises in long, slender, white needles, melting at 38°. It is sparingly soluble in water and light petroleum; readily soluble in most other solvents, and in cold hydrochloric acid and alkalis. The *phenylhydrazone* of propiononedicarboxylic acid, $N_2HPh{:}C_5H_8(COOH)_2$, crystallises from alcohol in pale-yellow, microscopic crystals, melts at 114·5°, and is insoluble in water, benzene, light petroleum, and chloroform, soluble in ether, and readily soluble in alcohol, acetone, and acetic acid. On heating with excess of hydriodic acid (sp. gr. = 1·7) and the theoretical quantity of amorphous phosphorus at 200—220° for many hours, the acid is converted into normal pimelic acid, hence it has the formula $CO(CH_2\cdot CH_2\cdot COOH)_2$. The author regards its formation from furfuracrylic acid by the splitting of the furfuran "ring" as an additional argument in favour of the view that furfuraldehyde has the formula  $\left\langle\begin{matrix}CH{:}C(COH)\\ -CH{:}CH-\end{matrix}\right\rangle O$, and not that ascribed to it by Baeyer.

Ethyl hydrogen propiononedicarboxylate, $COOH{\cdot}C_5H_8O{\cdot}COOEt$, is formed by boiling the ethyl salt with the calculated quantity of alcoholic potash. It crystallises in white needles, melts at 67—68°, and is insoluble in light petroleum, soluble in water, readily soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide. The *silver* salt, $C_9H_{13}O_5Ag$, decomposes very readily. The *phenylhydrazone*, $C_9H_{14}O_4{:}N_2HPh$, forms pale-yellow, microscopic crystals, melts at 112°, and is insoluble in water and light petroleum, readily soluble in ether, hot alcohol, benzene, and acetic acid.

On digestion with alcoholic ammonia, either for some hours at 100° or for a short time at 150°, ethyl propiononedicarboxylate is converted into a compound, $C_7H_{10}O_2N_2$, which is probably symmetrical *imidopimelimide*. It crystallises from hot water in long, thick prisms, from alcohol in long, compact, white needles, begins to sublime rapidly at 250—260° without decomposition, melts at 292°, is sparingly soluble in the ordinary solvents, and decomposes when boiled with hydrochloric acid or alkalis into ammonia and propiononedicarboxylic acid.

Ethyl furfuracrylate, $C_4H_3O{\cdot}CH{:}CH{\cdot}COOEt$, is prepared by heating furfuropropionic acid with an equal weight of alcohol and one-fourth its weight of sulphuric acid for four hours at 100°. It is a colourless oil of pleasant odour and bitter taste, boils at 228—230° without decomposition, and is insoluble in water but miscible with alcohol and ether. W. P. W.

Furfuralmalonic Acid. By W. Marckwald (*Ber.*, **21**, 1080—1083).—*Diethyl furfuralmalonate*, $C_4H_3O{\cdot}CH{:}C(COOEt)_2$, is obtained by heating a mixture of furfuraldehyde and ethyl malonate with acetic anhydride; the product is a slightly yellow, thick oil, with an ethereal odour and sharp bitter taste. It is insoluble in water, but mixes with alcohol and other solvents in all proportions.

Furfuralmalonic acid, $C_4H_3O{\cdot}CH{:}C(COOH)_2$, obtained by hydrolysing the ethyl salt, crystallises from ether, alcohol, or glacial acetic acid in compact prisms, which melt at 187° with decomposition, are readily soluble in water, but insoluble in benzene, light petroleum, and chloroform. When heated above its melting point, carbonic anhydride is evolved, and furfuracrylic acid is obtained. The salts are mostly readily soluble.

Monethyl furfuralmalonate, $C_4H_3O{\cdot}CH(COOH){\cdot}COOEt$, is formed by gently heating the diethyl salt for a short time with an excess of potash; it crystallises from benzene in large, thick, transparent, slightly yellow, rhombic prisms, melting at 102·5°. It is very sparingly soluble in cold, more readily in hot water, dissolves tolerably readily in benzene and chloroform, but is insoluble in light petroleum. When distilled, it yields carbonic anhydride and ethyl furfuracrylate. The alkaline salts are readily, those of the alkaline earths and the heavy metals only sparingly, soluble.

Furfuralmalonamide, $C_4H_3O{\cdot}CH{:}C(COONH_2)_2$, is obtained by the action of concentrated ammonia on diethyl furfuralmalonate. It is tolerably readily soluble in hot water and boiling alcohol, from which it crystallises in white needles, melting at 180° with decomposition; it dissolves very readily in glacial acetic acid, but is insoluble in ether, benzene, light petroleum, and chloroform. On boiling with hydrochloric acid, it yields ammonia and furfuralmalonic acid.

Furfurylmalonic acid, $C_4H_3O{\cdot}CH_2{\cdot}CH(COOH)_2$, is formed when furfuralmalonic acid is reduced with sodium amalgam. It is readily soluble in water, ether, glacial acetic acid, and alcohol, from which it crystallises in long, slender, colourless needles, melting at 125°, but it is almost insoluble in light petroleum, benzene, and chloroform. When distilled, it gives carbonic anhydride and furfuropropionic acid. Most of the salts are soluble in water. F. S. K.

Hexahydropseudocumene and its Relation to Mononaphthene. By M. KONOVALOFF (*Chem. Centr.*, 1887, 1133, from *Zurn. russk. obšč.*, 1887, 255—257).—Pure *hexahydropseudocumene*, the product of the action of hydriodic acid and phosphorus on pseudocumene, boils at 135—138°, and has sp. gr. 0·7812 at 0°, and 0·7667 at 20° (water at 0° = 1). *Nononaphthene*, prepared by Markownikoff and Ogloblin, boils at 135—136°, and has a sp. gr. 0·7808 at 0°, and 0·7652 at 20°.

Both these compounds behave in the same way towards nitric acid, a small quantity of a crystalline compound showing the melting point of trinitrocumene being the only product. With bromine in presence of aluminium bromide, they both react in the same way with formation of tribromopseudocumene and resinous substances. J. W. L.

Action of Titanium Chloride on Phenol. By A. SCHUMANN (*Ber.*, **21**, 1079—1080).—*Phenyl orthotitanate hydrochloride*,

$$Ti(OPh)_4,HCl,$$

is obtained by acting on phenol in anhydrous benzene solution with titanium chloride, and crystallising the product from benzene. It decomposes on exposure to moist air, and yields phenol, titanic acid, and hydrochloric acid when treated with water. F. S. K.

Nitrosonitroresorcinol. By C. DE LA HARPE and F. REVERDIN (*Ber.*, **21**, 1405—1407).—*Nitrosonitroresorcinol*, $OH{\cdot}C_6H_2O(NO_2){:}NOH$ [$OH : NO_2 : O : N{\cdot}OH = 1 : 2 : 3 : 4$], is obtained by adding an excess of dilute sulphuric acid to a cooled mixture of nitroresorcinol (m. p. = 85°), aqueous soda (10 per cent.), and sodium nitrite in equimolecular proportions. It crystallises in brown needles, does not melt at 200° but decomposes with explosion when heated beyond this temperature, and is readily soluble in water, acids, and alkalis, sparingly soluble in alcohol, and insoluble in benzene, ether, and chloroform. On reduction with tin and hydrochloric acid, it yields a diamidoresorcinol identical with that obtained from dinitrosoresorcinol. When treated in aqueous solution with ferrous sulphate or iron filings, it gives an intense green coloration owing to the formation of a dye which can be separated by the addition of salt. This, in an acid bath, dyes wool green. A mixture of nitrosonitroresorcinol and resorcinol dissolves in concentrated sulphuric acid with a green colour, which gradually changes through blue to violet. W. P. W.

Ethereal Oil of Asarum Europaeum L. By A. S. F. PETERSEN (*Ber.*, **21**, 1057—1064).—The oil obtained from *Asarum europaeum* is a thick, dark-brown, neutral liquid with a sweet, aromatic odour; it dissolves readily in ordinary solvents, and on long exposure to winter cold deposits crystals of asarone in considerable quantities. The oil can be separated into two chief portions by distilling with steam and subsequent fractioning. The fraction boiling about 175° contains a terpene, which was found to be identical with pinene. The fraction boiling at 240—260°, on further fractioning, yields a slightly yellow oil which boils at 247—253°, and has the formula $C_{11}H_{14}O_2$.

The halogens act energetically on this compound, and when heated with concentrated hydriodic acid it yields methyl iodide in quantities which show the presence of two methoxy-groups. Nitrous acid converts it into a compound, $C_{11}H_{14}O_2N_2O_3$, which crystallises in slender yellow needles, melting at 118°, insoluble in water, but soluble in glacial acetic acid and dilute alcohol. When oxidised with nitric acid, the oil yields a resinous product, oxalic acid, and small quantities of an acid melting at 178°, considerable quantities of carbonic anhydride and hydrogen cyanide being evolved. By careful oxidation with potassium permanganate, acetic acid, oxalic acid, and veratric acid are obtained with evolution of a considerable quantity of carbonic anhydride.

The chief constituent of asarum oil is therefore a compound which has probably the constitution $C_6H_3(C_3H_5)(OMe)_2$ $[C_3H_5 : OMe : OMe = 1 : 3 : 4]$. The oil obtained from *Asarum canadense* L. also contains pinene, but differs from that of *Asarum europaeum*, inasmuch as considerable quantities of acetic acid are evolved when the oil is fractioned.
F. S. K.

Bromeugenol-derivatives. By E. v. BOYEN (*Ber.*, **21**, 1393—1397).—Dibromeugenol, obtained by the reduction of dibromeugenol dibromide in alcoholic solution with zinc-dust, dissolves readily in alkalis forming salts which crystallise in lustrous scales; the potassium, $C_3H_5{\cdot}C_6HBr_2(OMe){\cdot}OK$, sodium, and ammonium salts were prepared. The *acetyl*-derivative, $C_3H_5{\cdot}C_6HBr_2(OMe){\cdot}OAc$, crystallises from ether in large, colourless, hexagonal prisms, from alcohol in groups of silky prisms, and melts at 66°. Nitro-derivatives of dibromeugenol could not be obtained. The *methyl ether* is crystalline, has a low melting point, and on oxidation with chromic acid mixture or permanganate is converted into a *dibromodimethoxybenzoic acid*, $(OMe)_2{\cdot}C_6HBr_2{\cdot}COOH$. This crystallises from high boiling petroleum in slender, lustrous needles, from water in silvery scales, melts at 182°, and is sparingly soluble in water, soluble in alcohol, ether, and acetic acid. The *zinc* salt is characteristic, and forms radiating groups of silvery crystals, which are equally as soluble in cold as in hot water; the *silver* salt is crystalline, and decomposes on boiling with water.

Dibromeugenol dibromide does not form salts with alkalis, but yields amorphous products whose nature has not yet been determined. The *acetyl*-derivative, $C_3H_5Br_2{\cdot}C_6HBr_2(OMe){\cdot}OAc$, crystallises from alcohol in slender prisms, from ether in rhombic tables, melts at 91°, and is soluble in benzene and acetic acid, readily soluble in ether. The *benzoyl*-derivative crystallises from light petroleum in tufts of needles, melts at 113°, and is sparingly soluble in alcohol and ether, soluble in benzene and acetic acid. W. P. W.

Amidoisopropylbenzenes. By E. J. CONSTAM and H. GOLDSCHMIDT (*Ber.*, **21**, 1157—1162).—In order to compare Nicholson's cumidine (*Annalen*, **65**, 58) with the paramidoisopropylbenzene prepared by Louis (*Ber.*, **16**, 111), the authors have nitrated cumene from cumic acid with a mixture of nitric and sulphuric acids at the ordinary temperature, and reduced the nitro-derivative with zinc and hydrochloric acid. A mixture of two bases is obtained, and these can be partially separated by means of their oxalates, of which the less soluble melts at 157—158°, and the more soluble at 125—128°. The less soluble salt, on treatment with aqueous soda, yields a colourless oil, which rapidly becomes dark-coloured on exposure to light, has an aromatic odour, boils at 217—220°, and does not solidify at −20°. This amido-derivative can be converted into paraisopropylbenzoic acid, and is identical with Nicholson's compound. The *oxalate*, $(C_9H_{13}N)_2,H_2C_2O_4 + 2H_2O$, crystallises in white, silvery scales, melts at 159° with decomposition, and is very sparingly soluble in water; the *acetyl*-derivative, $C_9H_{11}\cdot NHAc$, crystallises in white, lustrous scales, and melts at 102—102·5°; and the *carbamide*-derivative, $CHMe_2\cdot C_6H_4\cdot NH\cdot CONH_2$, crystallises in slender, colourless needles, and melts at 152°. The base obtained by Louis' method also yields paraisopropylbenzoic acid, and, contrary to his statement, yields a crystalline oxalate and acetyl-derivative which are identical with the compounds just described, consequently the bases obtained both by Nicholson and Louis have the constitution $[NH_2 : Pr = 1 : 4]$.

The more soluble oxalate (m. p. = 125—128°) is a mixture of the oxalates of ortho- and para-amidoisopropylbenzene, and can be separated into its constituents by treatment with aqueous soda and fractional crystallisation of the acetyl-derivatives of the two bases. Orthamidoisopropylbenzene boils at 213·5—214·5° at 732 mm. pressure, and does not solidify in a freezing mixture. The *hydrochloride*, $C_9H_{13}N,HCl$, crystallises in large, colourless, seemingly rhombic prisms, which rapidly become opaque on exposure to the air; the *oxalate*, $(C_9H_{13}N)_2,H_2C_2O_4 + H_2O$, crystallises in long, colourless prisms and melts at 173°; the *acetyl*-derivative, $C_9H_{11}\cdot NHAc$, crystallises in tufts of colourless needles and melts at 72°; the *carbamide*-derivative, $CHMe_2\cdot C_6H_4\cdot NH\cdot CONH_2$, crystallises in small, white needles and melts at 133—134°. W. P. W.

Compounds of Alloxan with Aromatic Amines. By G. PELLIZZARI (*Chem. Centr.*, 1887, 1288 and 1396, from *L'Orosi*, **10**, 253—263 and 295—302).—Alloxan gives additive compounds with aromatic bases in aqueous solution which are not salts, as the base cannot be separated from them.

α-Naphthylaminealloxan, $C_{14}H_{11}N_3O_4$, is insoluble in water, sparingly soluble in ether, light petroleum, and chloroform; from alcohol it crystallises in slender, white needles. It is insoluble in acids and in ammonia, soluble in fixed alkalis, by which it is changed into a new acid, $C_{14}H_{10}N_2O_4$; this separates from dilute alcohol in long needles, is insoluble in ether, light petroleum, chloroform, readily so in alcohol and acetic acid. When boiled with alkali, the acid loses carbon dioxide and ammonia. β-Naphthylamine gives no additive product.

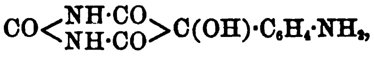
Anilalloxan, $C_{10}H_9N_3O_4$, crystallises from alcohol in needles which decompose at 248°. It is soluble in hot water. The compound behaves as an amido-acid, and forms salts both with alkalis and with acids. Fixed alkalis dissolve it with formation of a new acid, $C_9H_8N_2O_3$. This decomposes at 130°, crystallises from ethyl acetate in slender, white needles, is sparingly soluble in water and ether, readily so in alcohol; when boiled with alkalis, it loses carbonic anhydride and ammonia.

Orthotoluidinealloxan forms white needles which on heating decompose without melting. It has both acid and basic properties. With alkalis it forms a new acid. Paratoluidine does not react with alloxan.

Pseudocumindinealloxan forms a crystalline powder and yields a new acid when treated with alkalis.

Secondary bases form analogous alloxan compounds. *Methylanilalloxan*, $C_{11}H_{11}N_3O_4$, crystallises from water in white plates. The aqueous solution is decomposed by boiling. It yields salts with bases and with acids. Cold alkali solution decomposes it into carbonic anhydride, ammonia, and an acid which could not be obtained in a crystallised state. *Diphenylaminealloxan* separates from alcohol as a crystalline powder of feebly basic properties; with alkalis, it yields an acid. Tertiary bases also react with alloxan in the same way. *Dimethylanilalloxan* forms shining white crystals. It is very sparingly soluble in water, readily so in hot alcohol. It is more stable than anil- and methylanil-alloxan, and yields crystalline salts with acids.

Several salts of dimethylanilalloxan were prepared, amongst them the silver salt, $C_{12}H_{12}AgN_3O_4$. Dilute potash solution dissolves dimethylanilalloxan; acetic acid precipitates from this solution the compound $C_{10}H_{12}N_2O_3$. This crystallises from alcohol in needles, decomposing at 281°. It has acid properties. *Diethylanilalloxan* is prepared in a manner analogous to the dimethyl-compound, and has similar properties. The author concludes that the constitution of anilalloxan is expressed by the formula

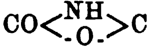


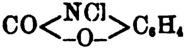
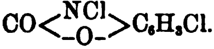
$$CO\!<\!\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}\!>\!C(OH)\cdot C_6H_4\cdot NH_2,$$

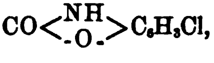
and that the other compounds have corresponding constitutions.

J. W. L.

Action of Chlorine on Carbonylorthamidophenol. By R. Jacoby (*J. pr. Chem.* [2], **37**, 28—52).—Carbonylorthamidophenol,

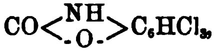


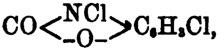
$CO\!<\!\begin{matrix}NH\\ \text{-}O\text{-}\end{matrix}\!>\!C_6H_4$, is best prepared by passing dry carbonyl chloride through dry benzene in which orthamidophenol is suspended, as long as a rise of temperature is observed. The residue obtained by evaporating the benzene is dissolved in water, treated with stannous chloride, boiled for a few minutes, and filtered. The nearly colourless filtrate deposits slightly reddish plates of carbonylamidophenol. It boils above 360°. When heated with hydrochloric acid above 150°, it takes up 1 mol. H_2O, and decomposes into carbonic anhydride and amidophenol. When the aqueous solution in presence of hydrochloric acid is gradually treated with a solution of bleaching powder, a crystalline precipitate is formed, consisting probably of a mixture of two chlorimides,  $CO<\begin{smallmatrix}NCl\\-O-\end{smallmatrix}>C_6H_4$ and  $CO<\begin{smallmatrix}NCl\\-O-\end{smallmatrix}>C_6H_3Cl$. When this is boiled with alcohol, carbonylchloramidophenol,

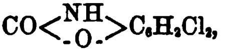


$$CO<\begin{smallmatrix}NH\\-O-\end{smallmatrix}>C_6H_3Cl,$$

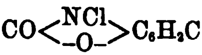
separates in large prisms melting at 192—193°. The same chlorinated compound is also formed by the action of water and of aniline on the mixed chlorimides.

Carbonyltrichloramidophenol,  $CO<\begin{smallmatrix}NH\\-O-\end{smallmatrix}>C_6HCl_3$, is obtained by passing chlorine through a solution of carbonylamidophenol in cold glacial acetic acid, and boiling the mixed chlorimides so formed with alcohol. It crystallises in needles, melts at 261—262°, and sublimes without decomposition when carefully heated. It is almost insoluble in cold solvents. A small amount of a compound melting at 184—186° is also formed in the reaction.

Carbonylchlorophenylchlorimide,  $CO<\begin{smallmatrix}NCl\\-O-\end{smallmatrix}>C_6H_3Cl$, is formed when a solution of bleaching powder is added to a solution of carbonylchloramidophenol in presence of hydrochloric acid. It melts at 119—120°. It is very readily soluble in ether, soluble in chloroform and benzene. Alcohol, water, aniline, and dimethylaniline decompose it, yielding carbonylchloramidophenol. When the dry chlorimide is heated, it melts, and directly afterwards explodes. When the substance is carefully heated in small quantities in a large flask, the decomposition takes place without violence, and the products can be collected. A compound was isolated, which was shown by analysis to be an isomeric dichloride.

α-Carbonyldichloramidophenol,  $CO<\begin{smallmatrix}NH\\-O-\end{smallmatrix}>C_6H_2Cl_2$, crystallises in sparingly soluble prisms melting at 270°; when heated with hydrochloric acid at 200°, it takes up 1 mol. H_2O, and decomposes into dichloramidophenol and carbonic anhydride. The ammoniacal solution yields a silver salt when treated with silver nitrate.

β-Carbonyldichloramidophenol is contained in small amount in the more soluble portions of the product obtained by heating carbonylchlorophenylchlorimide. It crystallises in lustrous needles melting at 213—214°, very readily soluble in alcohol, ether, and glacial acetic acid, less soluble in water.

α-Carbonyldichlorophenolchlorimide,  $CO<\begin{smallmatrix}NCl\\-O-\end{smallmatrix}>C_6H_2Cl_2$, prepared by precipitating a solution of α-carbonyldichlorimidophenol in glacial acetic acid with a solution of bleaching powder, begins to melt at 145—150° with decomposition. Boiling alcohol converts it quantitatively into carbonyldichlorophenol. It is very slowly decomposed by water. The *β-compound* forms white needles melting at about 89°. Cold alcohol decomposes it with evolution of chlorine. Both compounds explode when quickly heated.

Carbonyltrichlorophenolchlorimide, $C_7HCl_4NO_3$, crystallises in white needles, which begin to decompose above 130°, and detonate when heated quickly. Boiling water and boiling alcohol convert it quantitatively into carbonyltrichlorophenol.

Carbonyltetrachloramidophenol, $C_7HCl_4NO_2$, is obtained by carefully exploding small amounts of the chlorimide in a capacious flask. It melts at 220—237°, is soluble in alcohol, ether, and benzene, less soluble in water; it could not be obtained quite pure. Bleaching powder precipitates *carbonyltetrachlorophenolchlorimide* from the solution in glacial acetic acid.

Carbonylbromamidophenol (m. p. 186—187°) when treated with chlorine water, yields a *chlorimide*, $C_7H_3ClBrNO_2$, which melts at 118—120° and resembles the other chlorimides.

Carbonyldibromamidophenol, $C_7H_3Br_2NO_2$, obtained by the action of an excess of bromine-water on carbonylamidophenol, crystallises from alcohol in plates which melt at 243—245° with partial decomposition. It is insoluble in cold water. The *silver salt* forms white needles. The *chlorimide*, $C_7H_2Br_2ClNO_2$, crystallises in large needles melting at 120°. N. H. M.

Secondary Diamines containing an Ethylene-group. By A. Colson (*Bull. Soc. Chim.*, **48**, 799—802; compare this vol., p. 139).—*Ethylene orthoditolyldiamine*, $C_2H_4(C_7H_8N)_2$, is prepared by heating a mixture of orthotoluidine and ethylene bromide. It is crystalline, dissolves in ether (7 parts), cold alcohol (10 to 12 parts), and boiling water (300 parts). The alcoholic solution (not the aqueous) reacts with acidified methyl-orange. The *hydrobromide* forms white crystals soluble in 30 parts of boiling water; the *hydrochloride* is sparingly soluble. N. H. M.

Action of Nitrous Acid on some Organic Bases. Dinitrosobenzenylamidine. By W. Lossen and F. Mierau (*Ber.*, **21**, 1250—1256).—*Benzenylamidine nitrite*, $NH_2{\cdot}CPh{\cdot}NH,HNO_2 + H_2O$, is obtained by evaporating a neutral solution of benzenylamidine hydrochloride with sodium nitrite. It forms well-defined plates which lose their water of crystallisation, and are gradually decomposed at 64°; heated at a higher temperature, it yields benzonitrile, nitrogen, and water. It is readily soluble in water and alcohol, but insoluble in ether; it shows all the properties of a nitrite.

Dinitrosobenzenylamidinebenzenylamidine, $C_{14}H_{14}N_6O_2$, is formed by the action of nitrous acid on benzenylamidine in an acid solution. It crystallises in leaves which are sparingly soluble in cold water or alcohol, more readily in hot water, very readily in hot alcohol, but almost insoluble in ether. It explodes when heated at 178°, and is decomposed by an excess of acid with evolution of gas.

Potassium dinitrosobenzenylamidine, $C_7H_5KN_2(NO)_2$, is obtained by adding potash to a hot alcoholic solution of the preceding compound.

It crystallises in needles which are readily soluble in water, sparingly in alcohol, and insoluble in ether. In the dry state, the salt is very explosive, but in aqueous solution can be boiled without any decomposition taking place. An aqueous solution gives precipitates with barium chloride, lead acetate, and mercurous nitrate; ammonia, hydroxylamine hydrochloride, and methylaniline hydrochloride throw down precipitates of slender, colourless needles. The metallic precipitates are explosive in the dry state. An aqueous magenta solution produces a voluminous, dark-red precipitate.

Silver dinitrosobenzenylamidine, $C_7H_6Ag(NO)_2N_2$, is also very explosive. F. S. K.

Mixed Diazo-compounds. By H. GOLDSCHMIDT and J. HOLM (*Ber.*, **21**, 1016—1026).—*Diazobenzenebenzylamine*, $PhN_2{\cdot}NH{\cdot}CH_2Ph$, is formed by the action of diazobenzene chloride on benzylamine; it crystallises from hot light petroleum in pale-yellow, thin, transparent leaves, melting at 72°, and is readily soluble in ether, benzene, and alcohol. This compound, like its higher homologues, is very readily acted on by acids; when boiled with hydrochloric acid, it behaves like a mixture of diazobenzenebenzylamine and diazobenzylaniline.

Paradiazotoluenebenzylamine, $C_6H_4Me{\cdot}N_2{\cdot}NH{\cdot}CH_2Ph$, is obtained by the action of paradiazotoluene chloride on benzylamine; it forms slightly yellowish leaves melting at 77°, and is readily soluble in benzene, alcohol, and ether. When boiled with hydrochloric acid, it reacts like a mixture of diazobenzyltoluidine with a smaller quantity of diazotoluenebenzylamine.

Orthodiazotoluenebenzylamine is obtained in the form of a dark-yellow oil by the action of orthodiazotoluene chloride on benzylamine.

β-Diazonaphthalenebenzylamine, $C_{10}H_7{\cdot}N_2{\cdot}NH{\cdot}CH_2Ph$, is produced by the action of β-diazonaphthalene chloride on benzylamine; it separates from ether and benzene in brownish crystals melting at 110°.

New Method for Determining the Constitution of Mixed Diazoamido-compounds.—When the reaction product of diazobenzene chloride and benzylamine is dissolved in benzene, warmed for a few minutes with 1 mol. of phenyl isocyanate, and the benzene evaporated in a vacuum, a product is obtained which crystallises from alcohol in long, slender, snow-white needles melting at 119°. Analysis showed that this compound consists of 1 mol. of phenyl isocyanate in combination with 1 mol. of the diazoamido-compound. Two formulæ are possible for this substance, $NHPh{\cdot}CO{\cdot}N(CH_2Ph)N_2Ph$ and

$$NHPh{\cdot}CO{\cdot}NPh{\cdot}N_2{\cdot}CH_2Ph.$$

When boiled with hydrochloric acid, it yields benzylphenylcarbamide, phenol, and a small quantity of benzyl chloride, which shows that the first formula is the correct one. The diazoamido-compound is therefore *diazobenzenebenzylamine*.

Similarly, the condensation-product of paradiazotoluene chloride and benzylamine yields with phenyl isocyanate a compound $C_{21}H_{20}N_4O$, which crystallises from alcohol in slender, white needles melting at 115—116°. By boiling this substance with hydrochloric acid, benzylphenylcarbamide, paracresol, and a small quantity of benzyl chloride are obtained, showing that the diazoamido-compound is *paradiazotoluenebenzylamine.* From these experiments, it follows that the reaction between diazochlorides and benzylamine is normal.

Dis-paradiazotoluene-ethylamine, $NEt(N_2\cdot C_6H_4Me)_2$, is formed by the action of paradiazotoluene chloride on ethylamine. It crystallises from ether in bright-yellow, transparent needles which melt at 121° with copious evolution of gas; it is readily soluble in ether, benzene, and hot light petroleum, sparingly in ether and cold light petroleum. When boiled with dilute sulphuric acid, it yields paratoluidine, paracresol, ethylamine, ethyl alcohol, and nitrogen. F. S. K.

Substitution-products of Parazotoluene. By J. V. JANOVSKY and K. REIMANN (*Ber.*, **21**, 1213—1219; compare Abstr., 1887, 479).—Three substitution-products are obtained by the action of bromine on parazotoluene in glacial acetic acid solution.

Orthobromazotoluene, $C_6H_3\overset{4}{Me}\overset{2}{Br}\cdot\overset{1}{N_2}\cdot C_6H_4\overset{4}{Me}$, separates from the glacial acetic acid solution and, after recrystallising from alcohol, is obtained in golden-orange-coloured, rhombic plates melting at 139°.

Bromazotoluenesulphonic acid, $C_6H_3\overset{4}{Me}\overset{2}{Br}\cdot\overset{1}{N_2}\cdot C_6H_3\overset{4}{Me}\cdot\overset{3}{SO_3H} + 1\frac{1}{2}H_2O$, is formed by acting on the preceding compound with sulphuric acid containing sulphuric anhydride. It yields very characteristic salts which are mostly sparingly soluble in water. The *potassium* salt, $C_{14}H_{12}BrN_2\cdot SO_3K$, crystallises in rhombic prisms. The *sodium* salt forms large, anhydrous, shining, golden prisms. The *copper* and *cadmium* salts are yellow, crystalline compounds. Paratoluidineorthosulphonic acid and metabromoparatoluidine are obtained when the acid is treated with tin and hydrochloric acid.

Metabromazotoluene remains in the mother-liquor from the ortho-compound, and is precipitated on adding water. It crystallises from alcohol in small, orange-yellow leaflets which are readily soluble in ether, acetone, and benzene, and melt at 128°. When treated with alcoholic ammonia and hydrogen sulphide, a hydrazobromotoluene, melting at 113°, is obtained. It yields a sulphonic acid, the sodium, potassium, and copper salts of which are readily soluble, and the acid, when reduced with tin and hydrochloric acid, gives paratoluidinemetasulphonic acid [$Me : SO_3H : NH_2 = 1 : 3 : 4$] and orthobromoparatoluidine [$Me : Br : NH_2 = 1 : 2 : 4$], melting at 20—23°.

The bromazotoluenesulphonic acid previously described (*loc. cit.*) must have the constitution [$Me : Br : N_2 : SO_3H : Me = 4 : 3 : 1 : 3 : 4$].

Dimetadibromazotoluene, $N_2(C_6H_3BrMe)_2$ [$Me : Br : N = 1 : 2 : 4$], is contained in the mother-liquor from the metabromazotoluene. It is a yellow, crystalline compound melting at 75°. When reduced, it yields orthobromtoluidine melting at 25°. F. S. K.

Action of Carbonyl Chloride on Hydrazides. By M. FREUND and B. B. GOLDSMITH (*Ber.*, **21**, 1240—1244).—*Malonyl hydrazide*, $CH_2(CO\cdot NH\cdot NHPh)_2$, obtained by heating ethyl malonate or malonamide with phenylhydrazine, crystallises from dilute alcohol in white leaflets which melt at 187°, are insoluble in water, but dissolve readily in alcohol, chloroform, and glacial acetic acid. When heated with a benzene solution of carbonyl chloride, a compound, $C_{17}H_{12}N_4O_4$, is obtained which crystallises from glacial acetic acid in yellowish-coloured leaves melting at 205°; it is very sparingly soluble in water and alcohol, and only sparingly soluble in benzene.

Ethylmalonyl hydrazide, $CHEt(CO\cdot NH\cdot NHPh)_2$, prepared by heating ethylmalonamide with phenylhydrazine, crystallises from glacial acetic acid in white needles which melt at 233°; it is sparingly soluble in alcohol and insoluble in water. When treated with carbonyl chloride, it yields a compound, $C_{19}H_{16}N_4O_4$, which crystallises from glacial acetic acid or alcohol, and melts at 112—113°.

Oxalyl hydrazide and carbonyl chloride give a product, $C_{16}H_{10}N_4O_4$, which is not acted on by alkalis or concentrated hydrochloric acid, and crystallises in microscopic forms melting above 300°.

Acetyl hydrazide and carbonyl chloride yield a compound, $C_{16}H_{16}N_4O_4$, which crystallises from dilute alcohol in white prisms. It melts at 93—94°, and can be distilled without decomposition.

F. S. K.

Action of Carbamide on Hydrazines. By A. Pinner (*Ber.*, **21**, 1219—1227; compare Abstr., 1887, 1042; also Skinner and Ruhemann, this vol., p. 274).—Phenylurazole is formed by heating phenylsemicarbazide with carbamide (2 mols.) at 150—160°; also by heating a mixture of phenylhydrazine hydrochloride and biuret suspended in amyl alcohol.

Orthotolylsemicarbazide, $C_8H_{11}N_3O$, is produced when orthotolylhydrazine is heated with carbamide (2 mols.). It crystallises in flat, compact needles melting at 159—160°, is tolerably readily soluble in water, sparingly in alcohol, and insoluble in ether and benzene. It reduces Fehling's and ammoniacal silver solution.

Orthotolylurazole, $C_9H_9N_3O_2$, is obtained by heating tolylhydrazine hydrochloride with carbamide (4 mols.). It forms white leaflets which melt at 170° and dissolve readily in hot, tolerably readily in cold water. It dissolves in dilute alkalis and ammonia, forming reddish solutions.

Paratolylsemicarbazide crystallises in shining leaves melting at 157—158°. It is only sparingly soluble in cold water, but dissolves rather easily in alcohol and hot water. It reduces ammoniacal silver and alkaline copper solutions.

Paratolylurazole crystallises in slender, yellowish needles which melt at 274° with decomposition. It is very sparingly soluble in both hot and cold water.

α-Naphthylsemicarbazide, $C_{10}H_7NH\cdot NH\cdot CONH_2$, is formed when α-naphthylhydrazine hydrochloride and carbamide are heated together at 140°. It crystallises from boiling amyl alcohol in thin, shining, slightly brownish leaves which melt at 231° and are insoluble in water and ether. It is sparingly soluble in alcohol, benzene, ammonia, and dilute alkalis, and reduces Fehling's solution.

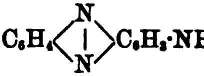
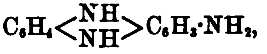
β-Naphthylsemicarbazide forms thin leaves which melt at 225° and towards solvents behaves like the α-compound.

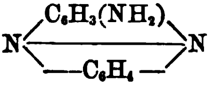
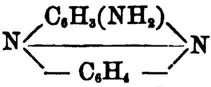
Nitrous acid has no action on phenylurazole; bromine and phosphorous pentachloride react only at a high temperature causing complete decomposition.

Dimethylphenylurazole, $C_8H_5Me_2N_3O_2$, was obtained in an impure state by heating the urazole with potash, methyl iodide, and a small quantity of methyl alcohol. It crystallises in white needles melting at 90°.

The *acetyl*-derivative, $C_8H_5Ac_2N_3O_2$, crystallises from benzene in white needles which melt at 141—149°, and are insoluble in water.

When phenylsemicarbazide is heated at 160—170° for four to five hours, ammonia, carbonic anhydride, carbon monoxide, and benzene are evolved and a brownish, vitreous mass remains. This residue consists chiefly of unchanged semicarbazide mixed with a considerable quantity of phenylurazole, but it also contains a new compound which remains behind in the form of a white, crystalline, granular mass when the residue is extracted with boiling water. This compound has the empirical formula $C_7H_6N_2O$; it melts at almost the same temperature as phenylurazole (264°) and, like the latter, dissolves readily in alkalis and ammonia; it is, however, very sparingly soluble in hot water, hot alcohol, and other solvents. It dissolves in ammonia without change, but when precipitated from its solution in soda it melts at 231°. F. S. K.

Phenosafranine. By P. BARBIER and L. VIGNON (*Bull. Soc. Chim.*, **48**, 338—342).—When a mixture of paraphenylenediamine and aniline (eq. mols.) is oxidised at a low temperature, a blue compound is obtained which changes gradually at the ordinary temperatures, instantly at 100°, into phenosafranine. Owing to its instability, the blue compound could not be analysed, but its conversion into phenosafranine is shown to take place without addition or elimination of any substance. It is converted by the action of zinc and hydrochloric acid at a low temperature into aniline and a new *leuco-base* which, when exposed to air, yields *amidophenazine*,  $C_6H_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_6H_3\cdot NH_2$, the *hydrochloride* of which crystallises in slender, violet-red needles. When this is reduced with zinc and hydrochloric acid, the leuco-base,  $C_6H_4<\begin{matrix}NH\\NH\end{matrix}>C_6H_3\cdot NH_2$, is obtained. By oxidising this leuco-base in presence of aniline at a low temperature, the blue compound is regenerated.

The constitutional formulæ,  $N\begin{matrix}C_6H_3(NH_2)\\ \hline C_6H_4\end{matrix}NCl\cdot C_6H_4\cdot NH_2$ and  $N\begin{matrix}C_6H_3(NH_2)\\ \hline C_6H_4\end{matrix}NCl\cdot NHPh$, are ascribed to safranine and to the blue compound respectively. N. H. M.

Alkylformanilides. By A. PICTET and P. CRÉPIEUX (*Ber.*, **21**, 1106—1111).—Alkylformanilides can readily be prepared by dissolving formanilide (1 mol.) in a small quantity of alcohol, adding the alkyl bromide (1 mol.), and finally an alcoholic solution of potassium hydroxide (1 mol.); the reaction takes place either in the cold or on gently warming. The method devised by Norton and Livermore (Abstr., 1887, 1038) for the preparation of methylformanilide cannot be employed for the preparation of its homologues, since sodium formanilide does not react either with ethyl bromide or with isopropyl bromide. The alkylformanilides are colourless, odourless, strongly refractive liquids, which do not solidify in a freezing mixture, boil at the same temperatures as the corresponding alkylacetanilides, and are insoluble in water, sparingly soluble in light petroleum, and readily soluble in the usual solvents. On distillation, they decompose slightly with formation on the one hand of carbonic oxide and the corresponding alkylaniline, and on the other of alcohol and benzonitrile or phenylcarbamine; when heated at 100° with alcoholic potash or concentrated hydrochloric acid, they are readily converted into the corresponding alkylanilines.

Methylformanilide boils at 253° under 716 mm. pressure, and has a sp. gr. = 1·097 at 18°; it could not, however, be solidified by prolonged cooling in a freezing mixture (compare Norton and Livermore, *loc. cit.*). The methylaniline and methylacetanilide obtained from it boiled at 191° and 253° respectively under 712 mm. pressure. *Ethylformanilide* boils at 258° under 728 mm. pressure, and has a sp. gr. = 1·063 at 16°; the corresponding ethylaniline boils at 203·5° under 712 mm. pressure and ethylacetanilide at 258° under 731 mm. pressure. Normal *propylformanilide* boils at 267° under 731 mm. pressure, and has a sp. gr. = 1·044 at 16°. The propylaniline derived from it boils at 219·5° at 716 mm. pressure, has a sp. gr. = 0·949 at 18°, and yields a nitrosamine which does not solidify in a freezing mixture (compare Döbner and v. Miller, Abstr., 1884, 1375); its acetyl-derivative boils at 266° under 712 mm. pressure, and crystallises from light petroleum or ether in large hexagonal scales melting at 47—48°. *Isopropylformanilide* boils at 261—263° under 720 mm. pressure. The corresponding *isopropylaniline* is a colourless liquid, which boils at 209—210° under 712 mm. pressure, and forms an oily nitrosamine and a platinochloride crystallising in thick, yellowish-red prisms; its *acetyl*-derivative boils at 262—263° under 712 mm. pressure, and crystallises from light petroleum in large, transparent tables having a camphor-like odour and melting at 39°. *Isobutylformanilide* boils at 274° under 731 mm. pressure. The isobutylaniline derived from it boils at 229—230° under 716 mm. pressure, and has a sp. gr. = 0·94 at 18°; its acetyl-derivative boils at 272—273° under 712 mm. pressure, and does not solidify in a freezing mixture. *Isoamylformanilide* does not solidify at −12°, boils at 285—286° under 728 mm. pressure, and has a sp. gr. =1·004 at 16°. The corresponding isoamylaniline boils at 252·5° under 730 mm., and at 244·5° (uncorr.) under 712 mm. pressure, has a sp. gr. = 0·928 at 15°, and yields an acetyl-derivative boiling at 287° under 730 mm. pressure. *Benzylformanilide* decomposes on distillation into carbonic oxide and benzylaniline. The determinations of the boiling points were made with the thermometer immersed in the vapour, and the specific gravity determinations are referred to the density of water at 4°.

Acetanilide boils at 301·5° (corr.) under 725 mm. pressure.

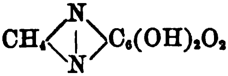
W. P. W.

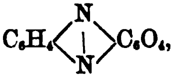
Benzoylaldehyde. By L. CLAISEN and L. FISCHER (*Ber.*, **21**, 1135—1140; compare Abstr., 1887, 940).—When an ethereal solution of benzoylaldehyde is treated with a solution of ammonium acetate in acetic acid, a derivative, $C_{18}H_{15}NO_2$, is obtained, which crystallises in bright-yellow, hair-like needles, melts at 219—220°, and is sparingly soluble in all the ordinary solvents. The *methylanilide* of benzoylaldehyde, $C_9H_7O{\cdot}NMePh$, forms compact white crystals melting at 103°, and the *benzylanilide*, $C_9H_7O{\cdot}NPhC_7H_7$, forms yellowish-white crystals, and melts at 130°. The *benzeneazo*-derivative,

$$COH{\cdot}CHBz{\cdot}N_2Ph,$$

crystallises in yellowish-red prisms, and melts at 103°. When treated with phenylhydrazine, benzoylaldehyde yields a white, crystalline *phenylhydrazone*, $CH_2Bz{\cdot}CH{:}N_2HPh$, melting at 118—120°, which on distillation yields a diphenylpyrazole identical with that prepared by Beyer and Claisen (Abstr., 1887, 944).

The authors have failed to obtain the acetal of benzoylaldehyde by heating a mixture of ethyl orthoformate and acetophenone either alone or with acetic anhydride, but find that it reacts with acetic chloride even in the cold with the formation of triphenylbenzene. The reaction is in some way dependent on the presence of these three compounds, since triphenylbenzene is not formed when acetophenone is treated with acetic chloride, with ethyl orthoformate, or with a mixture of ethyl formate and acetic chloride. W. P. W.

Benzenetriphenazine. By NIETZKI and A. W. SCHMIDT (*Ber.*, **21**, 1227—1230; compare Nietzki and Kehrmann, Abstr., 1887, 473).—*Dihydroxyquinonephenazine*,  $CH_4\langle\overset{N}{\underset{N}{|}}\rangle C_6(OH)_2O_2$ [OH : O : O : OH = 1 : 2 : 3 : 4], is produced when a solution of sodium rhodizonate in dilute hydrochloric acid is mixed with an equivalent quantity of an orthophenylenediamine salt. It forms reddish-brown needles, which dissolve in dilute alkalis with a violet colour, but are sparingly soluble in acetic acid and indifferent solvents.

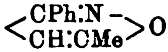
Diquinoylphenazine,  $C_6H_4\langle\overset{N}{\underset{N}{|}}\rangle C_6O_4$, is formed by the action of oxidising agents, such as dilute nitric acid, ferric chloride, &c., on the preceding compound. It exists only as the hydrate, and when dried at 100° has the composition $C_{12}H_4N_2O_4,3H_2O$; it forms slightly yellowish needles, which are only sparingly soluble in water and acetic acid. It is decomposed when boiled with water, and is converted into dihydroxyquinonephenazine when treated with sulphurous acid.

Benzenetriphenazine, $C_6(N_2C_6H_4)_3$, is obtained by warming diquinoylphenazine (1 mol.) with a dilute, aqueous solution of orthophenylenediamine sulphate (2 mols.). It is only sparingly soluble in most solvents, but dissolves rather easily in hot aniline; this solution on cooling deposits reddish-brown needles, which consist of benzenetriphenazine in loose combination with aniline. On washing with alcohol or water, these crystals are resolved into their constituents. When the compound is dissolved in glacial acetic acid and a few drops of concentrated hydrochloric acid added, an orange-red salt is precipitated, but dissolves again on boiling. The solution, on cooling, deposits triphenazine in greenish-yellow needles which do not melt, but sublime partially without decomposition at a high temperature. It is a very feeble base, and combines only with very concentrated acids to form orange-yellow salts which are decomposed by water.

Orthophenylenediamine sulphonic acid and rhodizonic acid yield a *monazine*, $C_{12}H_5N_2O_4{\cdot}HSO_3$, crystallising in brownish-yellow needles which are soluble in hot water. F. S. K.

Action of Ethyl Oxalate on Acetophenone. By E. Brömme and L. Claisen (*Ber.*, **21**, 1131—1135).—When treated with aqueous alkalis, ethyl benzoylpyruvate decomposes for the most part into acetophenone, ethyl alcohol, and the corresponding oxalate (Abstr., 1887, 944), and a like decomposition occurs, although to a less extent, when a solution of potassium hydroxide in absolute alcohol is employed to effect the saponification. A good yield of benzoylpyruvic acid can, however, be obtained without the intermediate formation of the ethyl salt by adding a mixture of ethyl oxalate and acetophenone in molecular proportion to a warm alcoholic solution of sodium (2 at. props.), heating for half an hour, and after removal of the alcohol by distillation, treating the product with water. The solution of the sodium salt is then freed from any ethyl benzoylpyruvate or oxalyldiacetophenone by acidification with acetic acid, and the acid finally precipitated by the addition of hydrochloric acid. The authors consider it probable that the action of the acetophenone on the unstable double compound of ethyl oxalate with sodium ethoxide, $ONa{\cdot}C(OEt)_2{\cdot}C(OEt)_2ONa$, results in the formation of the compound $CHBz{:}C(ONa){\cdot}C(OEt)_2{\cdot}CNa$, which on treatment with water yields ethyl alcohol and disodium benzoylpyruvate. Benzoylpyruvic acid crystallises with 1 mol. H_2O in short, white prisms, melts at 156—158° with the evolution of carbonic anhydride, and is readily soluble in methyl and ethyl alcohol, sparingly soluble in benzene and water. It is a strong acid and forms with alkalis both normal and basic salts, the first of which are comparatively stable, whilst the latter when boiled with water decompose into acetophenone and the corresponding oxalate. Ferrous sulphate gives with dilute solutions of the sodium salt an evanescent, dark violet-red coloration, or with more concentrated solutions a dark-blue precipitate, which rapidly becomes greyish-blue, and finally brown; the *mercury* salt crystallising in colourless, lustrous, slender prisms is also characteristic. The *aniline*-derivative, $CH_2Bz{\cdot}C(NPh){\cdot}COOH$, crystallises in citron-yellow prisms, and melts at 168—170° with decomposition.

Oxalyldiacetophenone, $CH_2Bz\cdot CO\cdot CO\cdot CH_2Bz$, is best obtained by adding to a mixture of anhydrous ether and sodium ethoxide (2 mols.) free from alcohol and cooled at 0°, first acetophenone (2 mols.) and then ethyl oxalate (1 mol.), and allowing the product to remain for several days; the resulting yellow salt is then dissolved in water, and decomposed by treatment with acetic acid. It crystallises from chloroform or acetic acid in lustrous, long, yellow prisms, melts at 179—180°, and is sparingly soluble in alcohol, ether, benzene, and light petroleum. Alkalis dissolve it with a yellow colour, and its solutions give a dark brownish-red coloration with alcoholic ferric chloride. W. P. W.

Benzoylacetone. By L. Claisen and O. Lowman (*Ber.*, **21**, 1149—1157).—When the sodium salt of benzoylacetone is treated with hydroxylamine, a crystalline compound is obtained, which melts at 67—68°, and has all the properties of the compound described as an oxime by Ceresole (Abstr., 1884, 1167). On analysis, however, its composition is found to be $C_{10}H_9ON$, and on account of its great stability the authors ascribe to it the formula  $<\substack{\text{CPh:N}-\\ \text{CH:CMe}}>\text{O}$, regarding it as a derivative of a new class of compounds, the monazoles.

Homologues of benzoylacetone of the type CHRAcBz could not be obtained by prolonged digestion of sodium benzoylacetone with ethyl iodide and alcohol on a water-bath; whilst treatment of the ketone, first with alcoholic potassium ethoxide, and then with ethyl iodide, results in the formation of ethyl benzoate and ethylacetophenone. *Ethyl benzoylacetone*, $C_{12}H_{14}O_2$, can, however, be prepared by heating a solution of benzoylacetone in benzene with the equivalent quantity of sodium wire until the whole is converted into the sodium-derivative of the ketone, and then digesting the product with ethyl iodide; it is a colourless oil boiling at 265—270°.

Contrary to expectation, the authors find that acetic chloride does not react with the sodium-derivative of dibenzoylmethane, and in view of the fact that Fischer and Bülow's dibenzoylacetone is not further acted on by sodium in boiling toluene (Abstr., 1885, 1237), and that tribenzoylmethane does not yield a tetrabenzoyl-derivative when treated with sodium ethoxide and benzoic chloride, they suggest that the sodium-derivatives of diketones may have the formula $R\cdot CO\cdot CH{:}C(ONa)R'$. Further experiments are promised.

The remainder of the paper is devoted to a discussion of the theory of the formation of ethyl acetoacetate advocated by the authors (Abstr., 1887, 584, 944; compare also Armstrong, Proc., 1887, 79), and it is pointed out that the failure to obtain a condensation compound by the action of ethyl isobutyrate on ethyl oxalate in the presence of sodium (Wislicenus, *Ber.*, **20**, 3396), affords confirmatory evidence in favour of the theory, since ethyl oxalate cannot yield derivatives with secondary acids if the reaction proceeds, as the authors suppose, according to the equation $COOEt\cdot C(ONa)(OEt)_2 + CH_2R\cdot COOEt = COOEt\cdot C(ONa){:}CR\cdot COOEt + 2EtOH$.

W. P. W.

Phenylacetic Acid and Benzyl Cyanide. By A. Meyer (*Ber.*, **21**, 1306—1316).—*Methyl dinitrophenylacetate*,

$$C_6H_3(NO_2)_2{\cdot}CH_2{\cdot}COOMe,$$

crystallises from alcohol in long, yellowish needles, melting at 82°.

Methyl azobenzenedinitrophenylacetate,

$$C_6H_3(NO_2)_2.C(N{\cdot}NHPh){\cdot}COOMe,$$

is prepared by dissolving methyl dinitrophenylacetate (1 gram) in alcohol (25 grams), adding a solution of sodium acetate (5 grams) in a little water, and carefully treating the whole with a solution of the calculated amount of diazobenzene chloride. It crystallises from alcohol in golden-yellow needles, melting at 182°.

Benzylbenzyl cyanide, $CH_2Ph{\cdot}CHPh{\cdot}CN$, is obtained by treating benzyl cyanide with sodium dissolved in 10 parts of absolute alcohol; and after half an hour the product is heated for some hours at 120° with benzyl chloride. The whole is then treated with water, extracted with ether, and the oil obtained by evaporating the ether distilled; it crystallises from dilute alcohol in white needles readily soluble in ether, melts at 58°, and boils without decomposition at about 335°. Phenylacetamide (which melts at 156° and boils at 280° to 300°, not 181—184°, Weddige, *J. pr. Chem.* [2], 7, 100), and the *compound*, $CH_2Ph{\cdot}CHPh{\cdot}C(NH{\cdot}C_7H_7){:}NH$, are also formed in the reaction. The latter crystallises from glacial acetic acid in white needles of a silky lustre melting at 182°.

Benzylphenylacetic acid, $CH_2Ph{\cdot}CHPh{\cdot}COOH$, is prepared by boiling benzylbenzyl cyanide with a slight excess of alcoholic potash for $1\frac{1}{2}$ days. It dissolves readily in dilute alcohol and ether, and in much hot water, from which it crystallises in lustrous needles which melt at 91° and boil at 330—340°. The *silver salt* is an insoluble powder. The *calcium salt* with 1 mol. H_2O crystallises in white needles readily soluble in hot water and in alcohol. The *barium* and *zinc salts* are described. The *methyl salt* crystallises in needles melting at 34°; the *ethyl* and *propyl salts* are oils, and boil at 325° and 338—339° respectively. The *amide* crystallises in needles which melt at 133—134°, and dissolve readily in alcohol and ether.

Isonitrosobenzyl cyanide, $CN{\cdot}CPh{:}N{\cdot}OH$, is formed when a cooled alcoholic solution of sodium ethoxide and benzyl cyanide is saturated with nitrous acid. It crystallises from water in white plates which melt at 129°, and dissolve readily in alcohol, ether, and hot alcohol. The *silver salt*, $CN{\cdot}CPh{:}N{\cdot}OAg$, forms sparingly soluble yellow crystals. When the cyanide is saponified, isonitrosophenylacetic acid (m. p. 127—128°, Müller, Abstr., 1884, 1129) is obtained.

Benzylphenylacetic acid has the same constitution as Wurtz's dibenzylcarboxylic acid (*Annalen*, Suppl. 8, 51) and Oglialoro's phenylhydrocinnamic acid (Abstr., 1879, 641), to which lower melting points are ascribed.

N. H. M.

Derivatives of Orthophthalaldehydic Acid. By S. Racine (*Compt. rend.*, **106**, 947—949).—With carbamide, orthophthaldehydic acid readily forms a ureide which is deposited in slender needles even from very dilute solutions. It has the composition

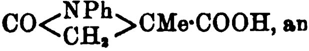
$$COOH\cdot C_6H_4\cdot CH{:}N\cdot CO\cdot NH_2,$$

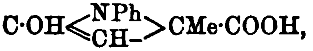
and is insoluble in cold water, alcohol, or ether, but dissolves readily in boiling water, and to a slight extent in boiling alcohol. It is easily soluble in alkaline hydroxides and carbonates, and when heated with sodium hydroxide it evolves ammonia. It melts at 240° with evolution of ammonia and formation of a yellow substance which has not yet been examined. The silver salt is readily soluble in boiling water from which it separates in slender needles. The barium and calcium salts are almost insoluble in water whether hot or cold. No dibromide was obtained by the action of bromine on the ureide. When the sodium salt is mixed with hydroxylamine hydrochloride, it yields benzaldoximo-orthocarboxylic acid (Abstr., 1887, 951).

When dibromophthalide and anhydrous sodium acetate are heated together, a neutral substance is obtained similar in all its properties to the substance which is formed by the action of acetic anhydride on the orthophthalaldehydic acid (*loc. cit.*). C. H. B.

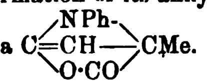
Derivatives of Phenylparacoumaric and Methylatropic Acids. By A. CABELLA (*Chem. Centr.*, 1888, 34, from *Rendi. Accad. Nap.* [2], **1**, 220—224).—*Silver phenylparacoumarate*, $C_{15}H_{11}O_3Ag$, is almost insoluble in water, and very stable. The *methyl* salt was obtained by passing dry hydrogen chloride through a solution of the acid in methyl alcohol, evaporating and crystallising the residue from weak alcohol; it forms white plates melting at 168—170°. The *ethyl* salt, $C_{17}H_{16}O_3$, melts at 151—152°, and is obtained by heating the silver salt of the acid with ethyl iodide at 110°.

Silver methylatropate, $C_{10}H_9O_2Ag$, is moderately soluble in hot water, but unstable. J. P. L.

Condensation Products from β-Anilido-acids. By A. REISSERT (*Ber.*, **21**, 1362—1391; compare Abstr., 1885, 900; 1886, 551).—Anilidopyrotartaric acid can most readily be prepared by heating ethyl anilidopyrotartaramate (50 grams) with potassium hydroxide (75 grams) and water (200 grams) in a reflux apparatus for 4 to 5 hours; the product is then boiled for half an hour without a condenser, acidified with hydrochloric acid, and converted into the copper salt which is then decomposed with hydrogen sulphide. It crystallises from water with 1 mol. H_2O, in lustrous, white prisms, melts at 111° in its water of crystallisation, and on further heating becomes solid, fusing again at 171° with decomposition. When it is heated at 180° for an hour in a closed tube, condensation ensues with the formation of pyranilpyroic anhydride, and a syrupy liquid from which the long, yellow needles of the former can readily be separated; these are then purified by crystallisation from dilute alcohol. Inasmuch as anilidopyrotartaric acid, $COOH\cdot CMe(NHPh)\cdot CH_2\cdot COOH$, yields the anhydride of pyranilpyroic acid, which on oxidation with permanganate, is converted into anilosuccinic acid, $COOH\cdot C(NPh)\cdot CH_2\cdot COOH$, the author considers that pyranilpyroic acid probably has the formula  $\mathrm{CO}<\substack{\mathrm{NPh}\\ \mathrm{CH_2}}>\mathrm{CMe{\cdot}COOH}$, and that it assumes the labile form,



$$\mathrm{C{\cdot}OH}\leqslant\substack{\mathrm{NPh}\\ \mathrm{CH-}}>\mathrm{CMe{\cdot}COOH},$$

prior to the formation of its anhydride, which is regarded as a lactone of the formula .

Pyranilpyrolactone (pyranilpyroic anhydride) can also be obtained by heating citraconic acid and aniline in molecular proportion at 170° until the decomposition is complete. It is identical with Gottlieb's citraconanil (*Annalen*, **77**, 277), melts at 98°, and is slightly volatile with steam. It dissolves in alkalis forming alkaline salts of pyranilpyroic acid, and is soluble in hot mineral acids from which it crystallises unchanged on cooling. The *phenylhydrazide*,

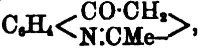
$$C_{11}H_{10}NO_2{\cdot}N_2H_2Ph$$

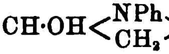
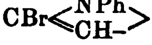
(compare Wislicenus, Abstr., 1887, 489), crystallises in small, lustrous, pure white needles, melts at 158—159°, and is readily soluble in alcohol and ether, but insoluble in water. The alkaline salts of pyranilpyroic acid decompose readily into aniline and citraconic acid when gently heated with mineral acids, and the acid decomposes in like manner when warmed with mineral acids or boiled with water. The *silver*, *lead*, *copper*, *tin*, *mercury*, and *iron* salts were prepared, and are sparingly soluble in water. On treatment with acetic chloride, acetic anhydride, phosphorus oxychloride, or phosphorus pentachloride, the acid is converted into pyranilpyrolactone; bromine does not react with it in the cold, and no definite product could be obtained from it by the action of sodium and ethyl iodide.

Anilsuccinic acid, $COOH{\cdot}C(NPh){\cdot}CH_2{\cdot}COOH$, is formed when pyranilpyroic acid (10 grams), dissolved in the calculated quantity of aqueous soda and mixed with 300 c.c. of water, is oxidised by potassium permanganate (18 grams) in 2 per cent. solution; after filtration, the product is treated with a solution of copper sulphate in the presence of sodium acetate, and the copper salt, after drying, is suspended in ether and decomposed by hydrogen sulphide. It crystallises in small, lustrous scales, melts at 151—152°, is readily soluble in alcohol and ether, soluble in benzene and water, sparingly soluble in light petroleum, and on boiling, its aqueous solution decomposes readily into acetic and oxanilic acids. The acid yields two series of salts, and of these *barium hydrogen anilosuccinate* crystallising in lustrous scales, and *sodium anilosuccinate* crystallising in small scales are the most characteristic; the normal salts can be dried at 100° without decomposition, but the hydrogen salts decompose when heated, yielding the corresponding salt of *β-anilpropionic acid*,

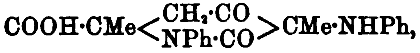
$$NPh{:}CH{\cdot}CH_2{\cdot}COOH.$$

This acid can readily be obtained from its copper salt by treatment with hydrogen sulphide, and crystallises from water in small needles, containing ½ mol. H_2O; these melt at 153° and dissolve readily in alcohol, ether, benzene, and chloroform, but only sparingly in light petroleum. It is more stable than anilosuccinic acid, but decomposes in an analogous manner into formanilide and acetic acid when boiled with acids or alkalis. The *barium*, with 1 mol. H_2O, *copper*, with 1 mol. H_2O, *lead*, with 1 mol. H_2O, and *silver* salts are crystalline. When heated for some time at 170°, both anilosuccinic acid and β-anilopropionic acid yield γ-ketodihydroquinoline (this vol., p. 277) in small quantity together with carbanilide and oxanilide, and by way of explanation the author assumes that β-anilpropionic acid, prior to condensation, undergoes intramolecular change with the formation of β-anilidoacrylic acid.

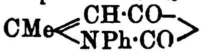
γ-Ketodihydroquinoline, when heated with acetic anhydride, forms an *acetyl*-derivative, $C_9H_6NO{\cdot}Ac$ [Ac = 1′], which crystallises from alcohol or acetic acid in small needles, melts at 228°, and is readily soluble in boiling alcohol, acetic acid, and ether, sparingly soluble in benzene and chloroform, and insoluble in light petroleum and water. The *hydrazone*, $C_9H_7N{:}N_2HPh$, crystallises from dilute alcohol in small, bright-yellow needles, melts at 168°, and is soluble in ether and alcohol. Since γ-ketodihydroquinoline does not undergo intramolecular change into the hydroxy-derivative [OH = 4′], the author is of opinion that ethyl anilacetoacetate (Conrad and Limpach, Abstr., 1887, 679) would not yield γ-hydroxyquinaldine if it had the constitution $NHPh{\cdot}CMe{:}CH{\cdot}COOEt$, and that consequently it must be regarded as ethyl β-anilbutyrate, $CMe(NPh){\cdot}CH_2{\cdot}COOEt$, which by condensation would yield the pseudo-form,  $C_6H_4<\begin{smallmatrix}CO{\cdot}CH_2\\N{:}CMe\end{smallmatrix}>$, and finally the hydroxy-derivative.

When dry pyranilpyroic acid, dissolved in hot acetic acid, is treated with zinc-dust, and the product after dilution with water and neutralisation is extracted with ether, *dihydropyranilpyroic acid*,  $CH{\cdot}OH<\begin{smallmatrix}NPh\\CH_2\end{smallmatrix}>CMe{\cdot}COOH$, is obtained. This crystallises in small, white needles, melts at 143°, and is soluble in alcohol and ether, sparingly soluble in benzene, chloroform, and water, and insoluble in light petroleum. It is far more stable than pyranilpyroic acid, and can be boiled with alkalis and mineral acids without decomposition. When heated above its melting point, or when treated with acetic chloride or acetic anhydride, it is converted into *dihydropyranilpyrolactone*, $C_{11}H_{11}NO_2$, which can also be obtained by distilling pyranilpyroic acid with zinc-dust in a current of carbonic anhydride. It forms small crystals, melts at 103°, dissolves readily in water, alcohol, ether, benzene, and chloroform, but only sparingly in light petroleum, and is converted into the acid without decomposition by boiling with alkalis. When treated with bromine-water, either in the cold or at 100°, dihydropyranilpyroic acid is converted into the *dibromide* of desoxypyranilpyroic acid, $C_{11}H_{11}NO_2Br_2$, a colourless, crystalline compound, which yields *bromodesoxypyranilpyroic acid*,  $CBr<\begin{smallmatrix}NPh\\CH-\end{smallmatrix}>CMe{\cdot}COOH$, when heated with aqueous soda. This melts at 165°, is readily soluble in alcohol and ether, sparingly soluble in water, and is destitute of basic properties; its *silver* salt crystallises in small, lustrous forms which rapidly decompose. *Desoxypyranilpyroic acid*, $C_{11}H_{11}NO_2 + 1\frac{1}{2}H_2O$, is obtained from the bromo-derivative by treatment with sodium amalgam and water, and forms small crystals which melt at 136°, and are soluble in alcohol and water, readily soluble in ether, and sparingly in benzene and light petroleum.

The compound which is obtained along with pyranilpyrolactone by the decomposition of anilidopyrotartaric acid at 180° has the formula $C_{20}H_{18}N_2O_3$, and is separated from the former by treatment with ether until the residue, consisting of small scales, is white and free from the lactone. It crystallises from absolute alcohol in lustrous, white prisms, or by the slow evaporation of its ethereal solution in colourless, monoclinic prisms; $a : b : c = 0{\cdot}5109 : 1 : 0{\cdot}8069$; $\beta = 89° 22'$; and is soluble in boiling alcohol and benzene, sparingly soluble in ether, and insoluble in water and light petroleum. When boiled with aqueous soda and the resulting solution neutralised with dilute sulphuric acid, it is converted into an acid, $C_{20}H_{20}N_2O_4$, which forms a white, microcrystalline powder, melts at 150°, and is readily soluble in excess of mineral acids, and in alcohol, ether, benzene, and acetone, sparingly soluble in water and chloroform, and insoluble in light petroleum and carbon bisulphide. The salts decompose readily, with the exception of the *sodium* salt, $C_{20}H_{19}N_2O_4Na$, which crystallises from water in silky scales. When dissolved in dilute sulphuric acid, and treated with a solution of potassium nitrite, it yields a compound, $C_{19}H_{17}N_3O_3$; this crystallises from absolute alcohol in lustrous, white needles, melts at 204°, and is readily soluble in benzene and chloroform, but sparingly soluble in alcohol, ether, and light petroleum. When the acid in boiling alcoholic solution is treated with sodium, it gives off an odour recalling that of the piperidine bases, and decomposes into aniline and a compound containing nitrogen. The author puts forward, under reserve, the view that these compounds are pyridine-derivatives, and ascribes to the acid the formula



$$\mathrm{COOH\cdot CMe}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{CMe\cdot NHPh},$$

regarding the compound $C_{20}H_{18}N_2O_3$ as its lactone, and the compound $C_{19}H_{17}N_3O_3$ as  $\mathrm{CMe}<\begin{matrix}\mathrm{CH\cdot CO\text{–}}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{CMe\cdot N(NO)Ph}$. This view derives some support from the fact that glycollic acid is also formed in the condensation of anilidopyrotartaric acid, rendering it probable that a portion of the latter, by taking up the elements of a molecule of water, breaks up into the former and α-anilidopropionic acid, which then undergoes condensation with a molecule of anilidopyrotartaric acid forming phenyldiketodimethylanilidopiperidinecarboxylic acid and its lactone. W. P. W.

Metallic Salts of Benzenesulphonic Acid. By T. H. NORTON and T. W. SCHMIDT (*Amer. Chem. J.*, **10**, 136—140).—The following salts are described:—$(PhSO_3)_2Cd + 7H_2O$; $(PhSO_3)_2Mn + 6H_2O$; $(PhSO_3)_2Ni + 6H_2O$; $(PhSO_3)_2Co + 6H_2O$, and $PhSO_3Hg$; with the exception of the last, they are easily soluble in water. H. B.

Amine Salts of Benzenesulphonic Acid. By T. H. Norton and J. H. Westenhoff (*Amer. Chem. J.*, **10**, 129—136).—No amine salts of the aromatic sulphonic acids have yet been described. The following derivatives of benzenesulphonic acid are all anhydrous, like the ammonium salts of the sulphonic acids, and unlike the metallic salts, which are generally hydrated; they are all readily soluble in alcohol and also in water, except the diphenylamine-derivative which is decomposed by water, and the orthotoluidine and α-naphthylamine salts which are only slightly soluble in cold water; they are generally insoluble in ether, benzene, or carbon bisulphide: those derived from the fatty amines are deliquescent: the dimethylaniline and methyldiphenylamine salts could not be obtained in the crystalline condition. The methylamine salt melts at 147°; dimethylamine salt at 110°; trimethylamine salt at 88—89°; ethylamine salt, 92°; diethylamine salt, 139°; triethylamine salt, 120—121°; isobutylamine salt, 132°; isoamylamine salt, 107°; phenylamine salt, 235—237°; diphenylamine salt, 115—117°; orthotoluidine salt, 137°; and the α-naphthylamine salt melts at 225°. H. B.

Amine Salts of Paratoluenesulphonic Acid. By T. H. Norton and A. H. Otten (*Amer. Chem. J.*, **10**, 140—145).—The free acid melts at 92°. Most of the amine salts are soluble in water; those of the aromatic amines crystallise easily, whilst the fatty amines yield salts which, on account of their greater solubility, are generally obtained only in radiocrystalline masses; the aromatic amine salts are more soluble in alcohol than the others, and have, moreover, a pronounced acid reaction, the others are neutral or alkaline. All are anhydrous. The methylamine salt melts at 125°; dimethylamine salt at 78°; trimethylamine salt at 92°; ethylamine salt at 11°; diethylamine salt at 88°; triethylamine salt at 65°; phenylamine salt at 223°; diphenylamine salt at 64°; orthotoluidine salt at 180°; and the α-naphthylamine salt melts at 239°. H. B.

Sulphimido-compounds. By P. T. Cleve (*Ber.*, **21**, 1099—1100; compare Abstr., 1887, 832),—Further experiments have shown that by the action of hydriodic acid on the chlorides of nitrosulphonic acids, the SO_2Cl-group is attacked, the nitro-group remaining intact.

The reaction product of bromine and metanitrobenzenesulphonic chloride is a compound which yields metanitrobenzenesulphonamide when treated with ammonia, and metanitrobenzenesulphonic acid when acted on by dilute alcohol.

Diphenyl disulphide, $(C_6H_5)_2S_2$, melting at 61°, is formed by the action of hydriodic acid on benzenesulphonic chloride; similarly the chloride of β-naphthalenesulphonic acid yields β-dinaphthyl disulphide, melting at 139°. F. S. K.

2′-Phenylindole. By E. Fischer and T. Schmitt (*Ber.*, **21**, 1071—1077).—The product obtained by Möhlau from aniline and bromacetophenone, and the compound obtained by Fischer (Abstr., 1886, 8 5) from acetophenonephenylhydrazone are both identical with 2′-phenylindole (compare Möhlau, this vol., p. 483). They all melt at 186°, give the same violet-blue, pine-wood reaction, the same nitroso-product and the same amidophenylindole melting at 174°.

Phenylacetaldehydephenylhydrazone, $CH_2Ph\cdot CH\!:\!N_2PhH$, is obtained by mixing phenylhydrazine with phenylacetaldehyde, and warming the mixture; it crystallises from light petroleum in almost colourless forms, melting at 58°, and readily soluble in alcohol, ether, and benzene.

2′-Phenylindole is produced by heating the preceding compound with zinc chloride for 5 to 10 minutes at 180—185°; it crystallises from hot alcohol or benzene in thin leaves melting at 186°. This compound resembles methylketole in all its reactions, except in its behaviour towards nitrous acid.

Nitroso-2′-phenylindole, [Ph : NO = 2′ : 3′] (Möhlau, Abstr., 1883, 342; Fischer, Abstr., 1886, 805), is best obtained by saturating a glacial acetic acid solution of the indole with a very concentrated solution of sodium nitrite. On heating quickly, it becomes darker coloured about 250°, and melts, not quite constantly, at about 258°, with decomposition. It is readily soluble in potash or soda, and is reprecipitated on addition of hydrochloric acid. It does not give Liebermann's reaction, but on reduction yields an amido-base, which has the closest resemblance to amidomethylketole (Wagner, this vol., p. 284).

Amido-2′-phenylindole, [NH_2 = 3′], is produced when the nitroso-compound is reduced with zinc and hydrochloric acid; it crystallises from hot benzene in thin, colourless, shining scales, which melt at 174°, and are almost insoluble in water, but dissolve readily in alcohol, ether, benzene, and dilute acids. It reduces Fehling's solution on boiling, and colours pine-wood orange. When in a moist condition, it is converted into a violet dye by oxidising agents, even by the oxygen of the air.

Benzylidene-2′-phenylindole, $CHPh(C_{14}H_{10}N)_2$, is formed by heating the indole with benzaldehyde; it crystallises from hot acetone in slender, shining needles, which melt at 262—263°, and are very sparingly soluble in alcohol.

Hydro-2′-phenylindole, $C_{14}H_{13}N$, is obtained by boiling the indole with zinc and hydrochloric acid; it separates from light petroleum in almost colourless crystals, which melt at 46°, are readily soluble in dilute mineral acids, and colour pine-wood orange. Nitrous acid converts it into a nitrosamine. F. S. K.

Metaditolyl. By E. Stolle (*Ber.*, **21**, 1096—1099).—*Metaditolyl*, $MeC_6H_4\cdot C_6H_4Me$, can be prepared by the action of nitrous acid and alcohol on orthotolidine, by heating orthodicresol with zinc-dust, or by the reduction of dichloroditolyl. It is a yellowish oil, boiling at 289°; its sp. gr. = 0·9993 at 16° (water at 4° = 1).

Dichloroditolyl, $C_6H_3MeCl\cdot C_6H_3MeCl$, is obtained from orthotolidine by Sandmeyer's method; the intermediate copper compound, $C_{12}H_6Me_2N_4Cl_2,CuCl$, is a dark, yellowish-brown powder. Dichloroditolyl crystallises from alcohol in white, shining leaves, melting at 51°. On oxidation with chromic acid, it yields chlorotoluylic acid, melting at 205°. When heated with phosphorous pentachloride, a compound, $C_{11}H_{10}Cl_4$, is formed, which on oxidation with dilute nitric acid yields *dichlorodiphenylmetacarboxylic* acid,

$$COOH{\cdot}C_6H_3Cl{\cdot}C_6H_3Cl{\cdot}COOH\ [(COOH)_2 : Cl_2 = 3 : 3' : 4 : 4'].$$

This acid is readily soluble in hot, sparingly in cold water, and melts at 267—268°.

Di-iododitolyl, $C_6H_3MeI{\cdot}C_6H_3MeI$, obtained by Sandmeyer's method, crystallises in yellow needles melting at 99—100°. F. S. K.

Aldines. By E. BRAUN and V. MEYER (*Ber.*, **21**, 1269—1282; compare this vol., p. 366).—Tetraphenylaldine* (Polonowska, this vol., p. 485) is prepared by gradually adding 5 per cent. sodium amalgam to a solution of benziloxime in aqueous soda. The product is filtered, washed with water, dried over sulphuric acid, and then rubbed with cold alcohol; it is again filtered, well washed with alcohol, dissolved in chloroform, and precipitated with alcohol. Finally it is dissolved in much boiling alcohol, from which it separates in slender, matted needles, melting at 245—246°. It is sparingly soluble, except in chloroform. Sulphuric acid dissolves it without change, yielding an intensely orange-coloured solution. It is not a base. The *tetranitro-derivative*, $C_{28}H_{16}N_6O_8$, melts at 130°—140°, dissolves in chloroform and benzene, and is insoluble in ether, alcohol, and light petroleum.

An attempt was made to prepare diphenylaldine by reducing isonitroso-acetophenone with stannous chloride and hydrochloric acid. *Eso-amidoacetophenone hydrochloride*, $COPh{\cdot}CH_2{\cdot}NH_2,HCl$, is formed. This salt separates from its aqueous solution in crystals melting at 183—184°. The *platinochloride* crystallises in long, slender, yellow needles melting at 200°. The *aurochloride* crystallises from water containing alcohol in slender, gold-coloured needles. The *sulphate* forms long crystals. The free base could not be isolated, as it decomposes when dried with formation of the *compound* $C_{16}H_{14}N_2O$. This crystallises from alcohol in stellate groups of slender needles, melting at 118—119°; it is readily soluble in hydrochloric acid. When eso-amidoacetophenone hydrochloride is treated with ammonia, instead of soda, iso-indole (diphenylaldine), $C_{16}H_{12}N_2$, is obtained (compare Wolff, *Ber.*, **20**, 432). The above compound was prepared by the action of alcoholic ammonia on bromacetophenone (Städel and Kleinschmidt, Abstr., 659), and the two preparations compared.

Eso-amidoacetophenone is also formed by the action of ammonia on bromacetophenone.

When isonitrosomethyl ethyl ketone is reduced with stannous chloride and hydrochloric acid, a hydrochloride of a base is obtained not identical with tetramethylaldine; aldines of the fatty series are, therefore, not directly formed when isonitroso-ketones are reduced in acid solution. N. H. M.

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* Both the authors and Polonowska seem to have overlooked the fact that this substance is identical with the compound described as *ditolaneazotide* and as *tetraphenylazine* by Japp and Wilson (Trans., 1886, 827), and by Japp and Burton (Trans., 1886, 843, and 1887, 101).—ED.

Substitution in Benzoïn and in Analogues of Desoxybenzoïn and Benzyl Cyanide. By V. Päpcke (*Ber.*, **21**, 1331—1343).—Benzylated derivatives are obtained when the three tolyl cyanides are respectively treated with sodium ethoxide and benzyl chloride, hence the substitution of methyl in the phenyl-group in benzyl cyanide does not interfere with the displacement of one of the hydrogen-atoms of the methylene-group by an alkyl-radicle. Benzylated metatolyl cyanide, $C_6H_4Me{\cdot}CH(C_7H_7){\cdot}CN$, is an oil which, after long standing, crystallises in rectangular tables, melts at 53°, and boils at 350—360° with slight decomposition. On treatment with aqueous alkalis, it yields benzylated metatoluylacetic acid, which separates from all solvents as an oil slowly solidifying to a crystalline mass which melts at 79—80°. Benzylated orthotolyl cyanide is an oil, and boils at 340—350° with slight decomposition; the corresponding acid forms large crystals and melts at 95·5°. Benzylated paratolyl cyanide crystallises from alcohol in long, white needles, melts at 79°, and is insoluble in water, but soluble in alcohol; the corresponding acid crystallises from alcohol in small aggregates, melts at 105°, and is soluble in ether. It was not found possible to substitute a second benzyl-radicle for the remaining hydrogen-atom of the methylene-group in any one of these cyanides.

Benzoïn yields benzil only when acted on by sodium ethoxide, but forms a sodium-compound when its solution in benzene is treated with sodium; this derivative, however, contains more sodium than is required for the formula $CHPhBz{\cdot}ONa$. Acetylbenzoïn also, which melts at 83° and not at 75° (Zinin, *Annalen*, **104**, 120), does not react when treated with sodium ethoxide, but decomposes into its constituents, acetic acid and benzoïn. Lastly, *benzoïn isobutyl ether*, which can be prepared by heating benzoïn (10 grams), sodium (2 grams), alcohol (20 grams), and isobutyl bromide (20 grams) at 150° for four hours, and is an oil boiling at 240—245° under 110 mm. pressure, does not form a benzylated derivative when treated with sodium ethoxide and benzyl chloride; from this it follows that it is not possible to effect a substitution of an alkyl-radicle for the hydrogen-atom of the methylene-group in benzoïn and its ethers.

Diphenyl benzyl ketone, $C_6H_4Ph{\cdot}CO{\cdot}CH_2Ph$, is prepared by dissolving phenylacetic chloride and diphenyl in molecular proportion in carbon bisulphide, treating the mixture with aluminium chloride in the cold, and finally heating at 100° in a reflux apparatus to complete the reaction. It crystallises from acetic acid and alcohol in lustrous scales, melts at 150°, and is insoluble in water, sparingly soluble in ether and cold alcohol. The *benzylated* ketone, $C_6H_4Ph{\cdot}CO{\cdot}CHPh{\cdot}C_7H_7$, is obtained by the action of sodium ethoxide and benzyl chloride; it crystallises in long, white needles, melts at 158°, is sparingly soluble in alcohol, and when heated for five hours at 160° with hydroxylamine hydrochloride is converted into the *oxime*, $C_{27}H_{22}{:}N{\cdot}OH$, which crystallises in slender needles, and melts at 175°. On treatment with thiocarbonyl chloride, diphenyl benzyl ketone is converted into the compound $C_6H_4Ph{\cdot}CO{\cdot}CPh{:}CS$ (compare this vol., p 484); this has an intense yellow colour, melts at 320°, is insoluble in alcohol and ether, very sparingly soluble in chloroform, and dissolves in concentrated sulphuric acid with a green colour, which soon changes through violet to red, owing to the absorption of moisture.

Naphthyl benzyl ketone, $C_{10}H_7{\cdot}CO{\cdot}CH_2Ph$, obtained in like manner from naphthalene, yields the corresponding alkyl-derivatives when treated with sodium ethoxide and ethyl bromide, isobutyl bromide, and benzyl chloride respectively. The products are oils, which cannot be crystallised, and do not yield crystalline oximes.

Fluoryl benzyl ketone, $C_{13}H_9{\cdot}CO{\cdot}CH_2Ph$, obtained under like conditions from fluorene, crystallises in small, white tables, melts at 156°, and is sparingly soluble in alcohol and ether; the yield amounted to 5 per cent. only of the weight of fluorene employed. When treated with sodium ethoxide and benzyl chloride, it yields a *benzylated*-derivative, $C_{13}H_9{\cdot}CO{\cdot}CHPh{\cdot}C_7H_7$, which crystallises from alcohol in slender, matted needles, melts at 149—150°, and is insoluble in ether, very sparingly soluble in hot alcohol. Fluoryl benzyl ketone reacts with thiocarbonyl chloride forming an orange-yellow powder, insoluble in alcohol and ether, but readily soluble in chloroform and benzene; although it could not be purified sufficiently for analysis, it probably has the composition $C_{13}H_9{\cdot}CO{\cdot}CPh{\vdots}CS$, since it gives an intense colour reaction with concentrated sulphuric acid.

Acenaphthyl benzyl ketone, $C_{12}H_9{\cdot}CO{\cdot}CH_2Ph$, formed in like manner from acenaphthene, crystallises in pale-yellow scales, melts at 114°, and is readily soluble in hot alcohol; the yield amounted to 30 per cent. of the weight of acenaphthene employed. On treatment with sodium ethoxide and benzyl chloride, it is converted into the *benzylated* derivative, $C_{12}H_9{\cdot}CO{\cdot}CHPh{\cdot}C_7H_7$, which crystallises from alcohol in pale-yellow needles, and melts at 104°. In none of these ketones was it found possible to substitute an alkyl-radicle for the second hydrogen-atom of the methylene-group. W. P. W.

Negative Nature of Organic Radicles and the Question of the Existence of true Nitroso-compounds. By V. Meyer (*Ber.*, 21, 1291—1295).—The great analogy existing between ethyl malonate and acetoacetate on the one hand, and desoxybenzoïn and benzyl cyanide on the other was previously mentioned. The two latter compounds differ from the former in not yielding sodium compounds which can be isolated. Homologues of benzyl cyanide can be obtained by heating the cyanide with alkyl chlorides and solid potash. In like manner, derivatives of desoxybenzoïn can be prepared by using aqueous alcoholic potash. Desoxybenzoïn and benzyl cyanide are converted by nitrous acid into the isonitroso-derivatives,

$$COPh{\cdot}CPh{\vdots}N{\cdot}OH \text{ and } CPh{\cdot}C(N{\cdot}OH){\cdot}CN.$$

Methyldesoxybenzoïn, however, does not yield the nitroso-compound, $COPh{\cdot}CMePh{\cdot}NO$, but benzoic acid and acetophenoneoxime.

When diphenylacetonitrile is treated with amyl nitrite and sodium ethoxide the polymeride described by Anschütz and Romig (Abstr., 1886, 1033) is formed. It is probable that the nitroso-compounds (such as contain the group NO in direct combination with carbon) cannot exist; the pseudonitroles, the only class of compounds of which the nitroso-nature is generally undisputed, may be considered as nitrates of the acetoximes, a view supported by Scholl's experiments (this vol., p. 443); thus, the formula of propylpseudonitrole would be $CMe_2{:}N{\cdot}O{\cdot}NO_2$. (Compare this vol., p. 147.) N. H. M.

Negative Nature of Organic Radicles. Examination of Desoxybenzoïn. By V. Meyer and L. Oelkers (*Ber.*, **21**, 1295—1306).—Desoxybenzoïn is prepared as follows:—20 grams of benzoïn, 60 grams of 75 per cent. alcohol, and 10 grams of granulated zinc are heated in a water-bath, treated with 20 grams of 80 per cent. alcohol saturated with hydrogen chloride, and the whole boiled for 2 to 3 hours. 10 grams of alcohol containing hydrochloric acid is then added, the liquid reduced to half its bulk by evaporation, and poured off from the unchanged zinc. The desoxybenzoïn is precipitated by hot water, the water poured off (on cooling more desoxybenzoïn separates) and the desoxybenzoïn made to solidify by cold water. It is pressed between filter-paper, distilled and then crystallised several times from alcohol. It melts at 60° and boils at 320—322° (corr.). The yield of pure substance is 60 per cent. of the weight of the benzoïn used.

The introduction of alkyl-groups into desoxybenzoïn is carried out in the following manner:—A weighed amount of sodium is treated with absolute alcohol, the calculated amount of finely powdered desoxybenzoïn added, and the whole heated for two minutes on a water-bath. When cold, the alkyl-derivative is added and the mixture heated on a water-bath for 15 minutes.

Methyldesoxybenzoïn, $COPh{\cdot}CHMePh$, crystallises from alcohol, which dissolves it readily in long, slender needles, which melt at 53°, and boil at 317·5—318·5° (corr.). The *oxime*, $CHPhMe{\cdot}CPh{:}N{\cdot}OH$, crystallises in long, prismatic needles, melting at 120°. *Desoxybenzoïn oxime* crystallises similarly and melts at 98°.

Ethyldesoxybenzoïn, $COPh{\cdot}CHEtPh$, crystallises in long, slender needles, melts at 58° and boils at 323—324° (corr.). The hydroxylamine-derivative crystallises from alcohol in needles melting at 129—130°.

Isobutyldesoxybenzoïn, $C_4H_9{\cdot}CHPh{\cdot}COPh$, prepared from isobutyl bromide, crystallises in short needles rather less soluble than the methyl and ethyl compounds; it melts at 78° and boils at 329·5—330·5° (corr.) The hydroxylamine compound crystallises in prisms melting at 118°.

Benzyldesoxybenzoïn, $CH_2Ph{\cdot}CHPh{\cdot}COPh$ (from benzyl chloride) crystallises in short, slender needles melting at 120°. It is very sparingly soluble in cold alcohol. The *oxime* crystallises from dilute alcohol in needles of a silvery lustre melting at 208°.

Attempts to introduce two alkyl-groups into desoxybenzoïn and to introduce a second alkyl-group into the derivatives described above gave negative results.

When a slow stream of nitrous acid is passed through sodium desoxybenzoïn, benzil monoxime is found. (Wittenberg and Meyer, Abstr., 1883, 803.) The compound is most readily obtained by Claisen's method (Abstr., 1887, 575), by adding 1 gram of desoxybenzoïn and 0·6 gram of amyl nitrite to a well-cooled solution of 0·12 gram of sodium in 3 to 4 grams of absolute alcohol; after two days the product is poured into water, shaken with ether, acidified and then extracted with ether. The yield is 0·7 gram of pure isonitroso-compound.

Desoxybenzoïnacetic acid, COPh·CHPh·CH_2·COOH, is prepared by adding 4 grams of ethyl chloracetate to 5 grams of desoxybenzoïn, 0·7 gram of sodium, and 7 grams of alcohol. It dissolves readily in aqueous potash, less in soda, and crystallises from alcohol in small tabular crystals melting at 156°. The silver salt was prepared. (Compare Knovenagel, p. 706.) N. H. M.

Negative Nature of Organic Radicles. By R. RATTNER (*Ber.*, **21**, 1316—1322).—*Dibenzylacetoxime*, OH·N:C(C_7H_7)$_2$, forms yellowish crystals melting at 119·5°.

Dibenzyl dibenzyl ketone, CO(CHPh·C_7H_7)$_2$, obtained by the action of benzyl chloride on dibenzyl ketone in presence of sodium, forms lustrous crystals melting at 121·5°. It is insoluble in water, readily soluble in ether, chloroform, and carbon bisulphide.

Methyl diphenylacetate, $CHPh_2$·COOMe, crystallises from alcohol in plates melting at 59—60°. This salt and also methyl methylmandelate were treated with sodium ethoxide and isobutyl bromide, but with negative results.

Dibenzyl paraphenylene diacetonitrile, C_6H_4[CH(C_7H_7)CN]$_2$, is prepared in a manner similar to dibenzyl dibenzyl ketone. This when boiled with concentrated aqueous potash yields *potassium paraphenylenedibenzyldiacetate*. The *free acid* is obtained as a resin, and is purified by alternately boiling with calcium carbonate and precipitating with acid four or five times. It is a microcrystalline powder which melts at 251° and is insoluble in water, readily soluble in alcohol, ether, and chloroform. The *barium* and *silver* salts are described.

In the preparation of the nitrile an amorphous compound of the empirical formula $C_{14}H_{11}N_2$ is obtained. It is possibly formed by the condensation of 3 mols. of the cyanide with elimination of 2 mols. of hydrogen cyanide. It is insoluble in the usual solvents, soluble in hot phenol, and is very indifferent towards reagents.

Methyl phenylbenzoylacetate, COPh·CHPh·COOMe, is prepared by dissolving sodium in absolute alcohol, heating the product (after evaporating off the alcohol) at 200° in a stream of hydrogen; desoxybenzoïn dissolved in ether is added and heated at 200° until white fumes appear in the flask. The product is treated with ether and an excess of methyl chlorocarbonate, and heated on a water-bath. On adding water, an oil is obtained which is extracted with ether and dried over sulphuric acid. It cannot be otherwise purified, as when distilled it decomposes into stilbene, benzoic acid, and carbonic anhydride. If ethyl chlorocarbonate is used, stilbene is formed at once in large quantities. N. H. M.

Substitution in Organic Compounds containing Negative Radicles. By W. SCHNEIDEWIND (*Ber.*, **21**, 1323—1330).—V. Meyer has shown that one atom of hydrogen in the methylene-group present in benzyl cyanide and desoxybenzoïn can be displaced by an alkyl-group when either compound is treated with sodium ethoxide and an alkyl iodide (this vol., p. 147). This reaction has been extended by the author to compounds containing in their formulæ two methylene- or methenyl-groups united together and each united with a negative radicle, and it is found that the nitrile of cinnamic acid, the nitrile of phenylpropionic acid, ethyl succinate, ethyl levulinate, benzalacetophenone, benzylacetophenone, and the nitrile of dibenzylacetic acid do not yield benzylated derivatives when respectively heated with the calculated quantities of sodium ethoxide and benzyl chloride at 103° until all alkaline reaction has disappeared.

Benzylacetophenone, $COPh{\cdot}CH_2{\cdot}CH_2Ph$, could not be obtained by the action of aluminium chloride on a mixture of phenylpropionic chloride and benzene, but is formed by boiling benzalacetophenone in acetic acid solution with zinc-dust for 3 to 4 hours. It crystallises from alcohol in lustrous scales, melts at 72—73°, boils at above 360° without decomposition, and is insoluble in water, readily soluble in alcohol and ether. When oxidised with potassium permanganate, it yields carbonic anhydride and benzoic acid. The *oxime* crystallises in slender needles, melts at 87°, and is insoluble in water, readily soluble in alcohol and ether. The *phenylhydrazone* is an oil. The *isonitroso*-derivative, $COPh{\cdot}C(N{\cdot}OH){\cdot}CH_2Ph$, prepared by adding amyl nitrite (2 mols.) and then the ketone to sodium (2 at.) dissolved in 20 times its weight of alcohol, crystallises from ether in beautiful, pale-yellow forms, melts at 125—126°, and is readily soluble in alcohol and ether. Inasmuch as only one isonitroso-group could be introduced into the molecule of this compound, an attempt was made to prepare the di-isonitroso-derivative of the isomeric dibenzyl ketone but without success, since the product, which was formed in small quantity and crystallised in needles melting at 107—108°, contained too high a percentage of nitrogen.

The *nitrile* of dibenzylacetic acid, $CH_2Ph{\cdot}CH(CN){\cdot}CH_2Ph$, is prepared by heating dibenzylacetamide and phosphorus pentachloride in molecular proportion dissolved in phosphorus oxychloride at 100° until evolution of hydrogen chloride ceases. It crystallises in white scales, or, by slow evaporation of its solutions, in tables, melts at 89—91°, and is insoluble in water, readily soluble in alcohol and ether. *Dibenzylacetamide* crystallises in white needles, melts at 128—129°, and is readily soluble in alcohol and ether, sparingly soluble in hot water.

Benzylcarbamine, $CH_2Ph{\cdot}NC$, is obtained by heating pure benzyl iodide dissolved in toluene with twice its weight of silver cyanide in a reflux apparatus for 3 to 4 hours. The product has the odour of the carbamines, boils chiefly at 220—221°, the thermometer afterwards gradually rising to 231°, and is a mixture of the carbamine with some benzyl cyanide. On treatment with sodium ethoxide and benzyl chloride, it yields benzylated phenylacetic acid (derived from the benzyl cyanide) and benzylamine only, hence the hydrogen of the methylene-group in benzylcarbamine unlike that in benzyl cyanide, is not displaceable by an alkyl-group under these conditions.

W. P. W.

Negative Nature of Organic Radicles. By E. KNOEVENAGEL (*Ber.*, **21**, 1344—1354).—In the first portion of the paper, the author gives the details of the experiments in which acetonitrile, isobutyronitrile, the nitrile of mandelic acid, diphenylmethane, triphenylmethane, fluorene, and the nitro-derivatives of these hydrocarbons were respectively treated with sodium ethoxide and benzyl chloride with negative results (compare this vol., p. 147).

Phenylbenzylsulphone, $CH_2Ph{\cdot}SO_2Ph$, is readily obtained by treating sodium benzenesulphinate dissolved in dilute alcohol with benzyl chloride. It is crystalline, melts at 148°, and is insoluble in water, sparingly soluble in ether and cold benzene, and dissolves in 60 parts of cold or 7 parts of boiling alcohol. It does not react with sodium ethoxide and benzyl chloride.

Desylacetic acid (desoxybenzoïnacetic acid, compare Meyer and Oelkers, p. 703), $COPh{\cdot}CHPh{\cdot}CH_2{\cdot}COOH$, is best prepared by adding desoxybenzoïn (1 mol.) to a solution of sodium (1 mol.) in 10 times its weight of alcohol, treating the product with acetic bromide (1 mol.) and heating it for 10 to 15 minutes on a water-bath. The product is then boiled for two hours in a reflux apparatus with 10 to 15 per cent. aqueous potash, diluted with water, shaken with ether to remove unaltered desoxybenzoïn, and the acid finally precipitated by addition of hydrochloric acid to the aqueous solution. The *copper*, *silver*, *zinc*, *lead*, *calcium*, and *barium* salts were prepared.

β-Desylpropionic acid, $COPh{\cdot}CHPh{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is formed in like manner from desoxybenzoïn, sodium ethoxide, and ethyl β-iodopropionate. It crystallises from alcohol in slender, white, seemingly quadratic needles, melts at 136°, and is insoluble in water, readily soluble in ether and hot alcohol. The *silver*, *copper*, *zinc*, *barium* and *calcium* salts are described. The *methyl* salt, $C_{16}H_{15}O{\cdot}COOMe$, crystallises in colourless needles, melts at 63—64°, and is readily soluble in alcohol and ether, insoluble in water; the *ethyl* salt, $C_{16}H_{15}O{\cdot}COOEt$, crystallises in small, pale-yellow needles, melts at 33—34°, and is readily soluble in alcohol and ether. Hydroxylamine and phenylhydrazine react with the acid, yielding products which however could not be obtained in a state suitable for analysis.

α-Desylpropionic acid, $COPh{\cdot}CHPh{\cdot}CHMe{\cdot}COOH$, is obtained under like conditions from desoxybenzoïn, sodium ethoxide, and α-bromopropionic acid. It crystallises from alcohol in slender, colourless needles, melts at 213—215°, and is less soluble in alcohol and ether than the β-acid. The *silver*, *copper*, *zinc*, *calcium* and *barium* salts were prepared.

W. P. W.

Bidesyls. By E. KNOEVENAGEL (*Ber.*, **21**, 1355—1361).—*Bidesyl*, $COPh{\cdot}CHPh{\cdot}CHPh{\cdot}COPh$, is obtained, together with a small quantity of desylmalonic acid, by the action of sodium desoxybenzoïn (1 mol.) on ethyl bromomalonate (1 mol.) in alcoholic solution. It is also formed, together with isobidesyl, by heating desoxybenzoïn (1 mol.) with sodium (2 at. prop.) dissolved in 10 times its weight of alcohol, and adding to the cooled product an ethereal solution of iodine (½ mol.), and both compounds are formed when a mixture of desoxybenzoïn (1 mol.) and sodium ethoxide (1 mol.) in alcoholic solution is treated with desyl bromide (1 mol.). It crystallises from benzene in needles, melts at 254—255°, and is insoluble in water, ether, alcohol, acids, and alkalis. When heated with hydroxylamine hydrochloride in alcoholic solution at 160°, it yields a compound which does not contain nitrogen; this crystallises from alcohol in lustrous forms, and melts at 171—172°.

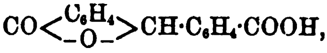
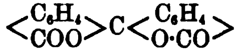
Isobidesyl crystallises in colourless prisms, melts at 160—161°, and is readily soluble in hot alcohol and benzene, sparingly soluble in ether and light petroleum. Like bidesyl, it is optically inactive, and both compounds when heated under like conditions boil almost simultaneously at about 340°. When boiled with hydroxylamine hydrochloride (3 to 4 mols.) and aqueous potash (2 mols.) on a water-bath in a reflux apparatus for four hours, isobidesyl is converted into a compound, $C_{56}H_{47}N_3O_4$, which melts between 110—120°, and is extremely soluble in cold alcohol, ether, and benzene, but insoluble in light petroleum. The research is being continued.

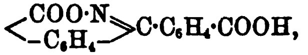
Desyl bromide, CHPhBr·COPh, can be obtained in almost quantitative yield by treating desoxybenzoïn with bromine by Staedel and Kleinschmidt's method for the preparation of bromacetophenone from acetophenone (Abstr., 1880, 659). It melts at 54—55°.

Ethyl bromomalonate, COOEt·CHBr·COOEt, is prepared by adding bromine (1 mol.) to ethyl malonate (1 mol.), distilling, and collecting the fraction boiling at 230—236°. W. P. W.

Diphthalylic Acid. By P. Juillard (*Chem. Centr.*, 1887, 1143—1145; *Arch. sci. phys. nat.* [3], **17**, 502—535, and **18**, 24—62).—Diphthalylic acid, $C_2O_2(C_6H_4{\cdot}COOH)_2$, is formed in good quantity by oxidising diphthallyl with potassic permanganate, or with potassic hypobromite or hypochlorite; it melts at 272°. The *ethyl* salt melts at 154°. If the acid is heated at about 110° with 40 per cent. caustic alkali, *hydroxydiphenylmethanetricarboxylic acid*,

$$OH{\cdot}C(C_6H_4{\cdot}COOH)_2{\cdot}COOH,$$

is formed, which, however, exists only in combination with bases; when liberated by the action of an acid, it is converted into the lactone. By heating the solution, *phthalidecarboxylic acid* is formed. With strong bases it deports itself as a tribasic acid, with ammonia and barium hydrate as a bibasic acid. The ethyl salt melts at 108°. Phosphorus and hydriodic acid reduce it to *diphenylmethanetricarboxylic acid*, $CH(C_6H_4{\cdot}COOH)_2{\cdot}COOH$, which crystallises with 1 mol. H_2O. At about 200° it melts, and at 250° is transformed into a beautiful, red substance melting at 260°. If diphthalylic acid is heated with 50 to 55 per cent. potash at 125—130°, *hydroxydiphenylmethanedicarboxylic acid*, $OH{\cdot}CH(C_6H_4{\cdot}COOH)_2$, is formed, which is transformed into the lactone on being liberated. The latter,  $CO\!<\!\begin{matrix}C_6H_4\\ -O-\end{matrix}\!>\!CH{\cdot}C_6H_4{\cdot}COOH$, melts at 205°. With potash and soda it acts as a bibasic acid, with ammonia as a monobasic acid only. The methyl salt melts at 154—155°, the ethyl salt at 99·5°. Alcoholic ammonia reacts with the ethereal salt with formation of an amide, $C_{14}H_9O_2{\cdot}CONH_2$, melting at 158—160°. With nitrosulphuric acid, a dinitro-acid is formed, melting at 270—280°. By oxidation with alkaline potassic permanganate, benzophenonedicarboxylic acid is formed, whilst chromic acid in glacial acetic acid oxidises phenylpthalidecarboxylic acid to a *dilactone*,  $<\substack{C_6H_4\\COO}>C<\substack{C_6H_4\\O\cdot CO}>$, which is also formed by heating benzophenonedicarboxylic acid either in the dry state or in solution. The salts of barium, copper, and silver, as well as the methyl and ethyl salts were prepared. It reacts with phenylhydrazine without loss of water. The hydroxylamine-derivative,



$$<\substack{COO\cdot N\\-C_6H_4-}>C\cdot C_6H_4\cdot COOH,$$

melts at 213—215°. The dilactone is extremely stable, and is only transformed into the acid when boiled with alkali. With fuming sulphuric acid it forms a sulphonic acid, which on fusion with potash gives alizarin. Aqueous and also alcoholic ammonia react with the dilactone, the former with production of an imide melting at 251—252°, the latter with production of a diimide which melts at 284—285°. Phenylphthalide mono- and di-carboxylic acids, and also the dilactone, are reduced by hydriodic acid and phosphorus at 170—180° with formation of *diphenylmethanedicarboxylic acid*,

$$CH_2(C_6H_4\cdot COOH)_2,$$

melting at 254—255°. If the temperature of the reaction with the dilactone is allowed to rise to 210—220°, anthranolcarboxylic acid is formed; this melts at 252—253°. J. W. L.

Derivatives of Orthotolidine. By P. L. Hobbs (*Ber.*, **21**, 1065—1068).—*Diacetylorthotolidine*, $C_{18}H_{20}N_2O_2$, crystallises from hot acetic acid in slightly-coloured needles which melt above 310°, and are only sparingly soluble in ordinary solvents. *Dibenzoylorthotolidine*, $C_{28}H_{24}N_2O_2$, crystallises from hot acetic acid in snow-white needles melting at 259°; it is insoluble in ordinary solvents. The condensation-product of orthotolidine and phthalic anhydride, $C_{30}H_{20}N_2O_4$, crystallises from benzene in dark-brown needles melting at 307°. The *urethane*, $C_{20}H_{24}N_2O_4$, crystallises from alcohol in large, pale-red needles melting at 187°. The *formyl*-derivative, $C_{16}H_{16}N_2O_2$, forms microscopic needles which melt at 254°; on distillation, a compound is obtained which melts at 121°, and has the properties of an amidine. *Tolyldithiocarbimide*, $C_{16}H_{12}N_2S_2$, crystallises from benzene in large, transparent plates melting at 157°.

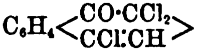
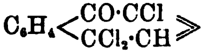
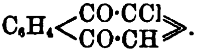
Orthodicresol, $C_{14}H_{14}O_2$, crystallises from water in slightly-coloured, large, broad needles melting at 157°.

Benzoylorthodicresol, $C_{28}H_{24}O_4$, crystallises from glacial acetic acid in long needles melting at 185°. The *acetyl*-derivative, $C_{18}H_{18}O_4$, forms long needles melting at 131°. The *ethyl*-derivative melts at 156°. The *propyl*-derivative crystallises from alcohol in snow-white leaves. The *amyl*-derivative crystallises from amyl alcohol in thick needles or prisms, which are readily soluble in alcohol and ether, and melt at 69°. (Compare Gerber, this vol., p. 484.) F. S. K.

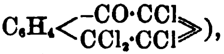
Action of Chlorine on Phenols. By T. Zincke (*Ber.*, **21**, 1027—1048).—*Ketochloride* is the generic name given to the ketone-like products obtained by the action of chlorine on phenols.

Dichlor-α-naphthol, $C_{10}H_5Cl_2{\cdot}OH$ [$OH : Cl_2 = 1 : 2 : 4$], is the first product which can be isolated of the action of chlorine on α-naphthol in glacial acetic acid solution; it is also formed by the reduction of tri- and penta-chloroketonaphthalene (see below). It crystallises from glacial acetic acid in thick, transparent needles, which lose acetic acid, become dull, and disintegrate on exposure to the air; it crystallises from benzene and alcohol in slender, shining needles, which melt at 107—108°, dissolve readily in ether, benzene, and absolute alcohol, and also in sodium carbonate with evolution of carbonic anhydride. It is readily oxidised by chlorine or bromine with formation of an insoluble, blue substance, which, on further treatment with the halogen, becomes yellow. This blue compound is also formed by the action of trichloroketonaphthalene. By careful oxidation with nitric acid, dichlor-α-naphthol yields chlor-α-naphthaquinone. The *acetyl-derivative*, $C_{10}H_5Cl_2{\cdot}OAc$, is readily soluble in glacial acetic acid and alcohol, and crystallises from the latter in thick, colourless needles, melting at 74—76°.

Trichlor-α-naphthol, [$Cl_3 = 2 : 3 : 4$], is obtained by reducing pentachloroketonaphthalene with alkaline sulphites; it crystallises from glacial acetic acid or benzene in long, colourless, silky needles, melts at 159—160°, is readily soluble in ether, less readily in warm, sparingly in cold alcohol or glacial acetic acid. The *acetyl-derivative* forms long, white, shining needles, which are moderately soluble, and melt at 123—124°. Trichlor-α-naphthol yields dichloro-β-naphthaquinone, and a small quantity of dichlor-α-naphthaquinone, when carefully oxidised with nitric acid in acetic acid solution, but with chromic acid the chief product is dichlor-α-naphthaquinone.

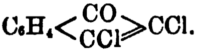
Trichlor-α-ketonaphthalene,  $C_6H_4{<}\begin{matrix}CO{\cdot}CCl_2\\CCl{:}CH\end{matrix}{>}$ or  $C_6H_4{<}\begin{matrix}CO{\cdot}CCl\\CCl_2{\cdot}CH\end{matrix}{\gg}$ (chlor-α-naphthaquinone chloride), is the second product of the action of chlorine on α-naphthol in glacial acetic acid solution; it crystallises in large, characteristic, transparent, flat, monoclinic prisms, melting at 120—121°, is very readily soluble in benzene, less so in glacial acetic acid, and sparingly in alcohol. This compound can also be obtained by the action of chlorine on dichlor-α-naphthol. When boiled with dilute alcohol or dilute acetic acid, it yields *chlor-α-naphthaquinone*,  $C_6H_4{<}\begin{matrix}CO{\cdot}CCl\\CO{\cdot}CH\end{matrix}{\gg}$. This crystallises from alcohol and dilute acetic acid in shining, yellow needles, which melt at 117—118°, and are readily soluble in benzene, sparingly in ether. When treated with chlorine in glacial acetic acid solution, it is converted into dichlor-α-naphthaquinone, and alkalis transform it slowly, with partial decomposition, into chlorohydroxynaphthaquinone. Treated with aniline, it yields chloranilido-α-naphthaquinone, which can also be obtained from dichloronaphthaquinone.

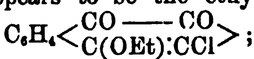
Trichloroketonaphthalene can be readily reduced to dichlor-α-naphthol, and when treated with aniline it yields anilidonaphthaquinonanilide. By the action of hydroxylamine hydrochloride on trichloroketonaphthalene, three different nitrogenous products are formed, two of which are insoluble in sodium carbonate; one of these is probably a true nitroso-compound, $C_{10}H_5Cl_2{\cdot}NO$ [NO : Cl_2 = 1 : 2 : 4]. The product which is soluble in sodium carbonate appears to be a *monoxime;* it melts at 146—149°, and decomposes at 170°. The third product is sparingly soluble, and melts at 205°.

Tetrachlor-α-ketonaphthalene, $C_6H_4{<}\begin{matrix}CO{\cdot}CCl_2\\ CCl{:}CCl\end{matrix}{>}$ (or dichlor-α-naphthaquinone chloride,  $C_6H_4{<}\begin{matrix}-CO{\cdot}CCl\\ CCl_2{\cdot}CCl\end{matrix}{\gg}$), was obtained in two different modifications, which perhaps have different constitutions as expressed by the above formulæ. Both compounds are formed by treating trichlor-α-naphthol with chlorine. The α-modification crystallises from glacial acetic acid in small, transparent rhombohedra, which, when taken from the solution, become yellow, and keep their colour when recrystallised from ether; it is rather easily soluble in hot alcohol or hot glacial acetic acid, and melts at 104—105°.

The β-modification crystallises from ether in shining, colourless, transparent, rhombic forms, which are combinations of prisms and pyramids; it melts at 93—94°, and becomes amethyst-coloured on exposure to light.

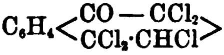
The β-modification can also be obtained by treating an alcoholic solution of the pentachloride (see below) with dilute alkali, or by boiling an alcoholic solution of the α-modification; in the latter case, dichlor-α-naphthaquinone is also formed.

These two modifications of tetrachlor-α-ketonapthalene are very similar in their general behaviour; they are both converted into dichlor-α-naphthaquinone when boiled with dilute alcohol or dilute acetic acid; when warmed with dilute alcoholic potash, they yield chlorhydroxynaphthaquinone, and when treated with concentrated potash and a few drops of alcohol, they are converted into dichlorindenehydroxycarboxylic acid, which can be recognised by transforming it into dichloroketoindene,  $C_6H_4{<}\begin{matrix}CO\\ CCl\end{matrix}{\gg}CCl$.

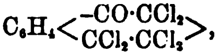
When potash is gradually added to a solution of the tetrachloride in absolute alcohol, long, orange-red shining needles, melting at 148—149°, are obtained. This compound, which can also be obtained from the pentachloride, appears to be the ethyl-derivative of chlorhydroxynaphthaquinone,  $C_6H_4{<}\begin{matrix}CO\text{——}CO\\ C(OEt){:}CCl\end{matrix}{>}$; it yields β-β-chlorhydroxy-β-naphthaquinone anilide when treated with aniline, and is converted into chlorhydroxynaphthaquinone by the action of alkalis.

The corresponding *propyl*-derivative is obtained by treating a propyl-alcoholic solution of the tetrachloride with potash in a similar manner; it is a yellowish-red, crystalline compound, which melts at 190°, and gives β-β-chlorhydroxynaphthaquinoneanilide when treated with aniline.

Tetrachloroketonaphthalene is converted into trichlor-α-naphthol by reducing agents; when treated with potassium iodide, iodine is liberated, amorphous insoluble compounds are obtained, and dichlorhydronaphthaquinone appears to be formed. It yields a mixture of various nitrogenous compounds when treated with hydroxylamine hydrochloride, and combines with aniline to form chloranilidonaphthaquinoneanilide (see below).

Pentachloroketohydronaphthalene,  $C_6H_4<\begin{matrix}CO - CCl_2\\ CCl_2\cdot CHCl\end{matrix}>$, is obtained by saturating a glacial acetic acid solution of α-naphthol with chlorine in the cold. It is readily soluble in hot benzene, from which it crystallises in colourless, almost right-angled, monoclinic plates, melting at 156—157°; it is very sparingly soluble in ether, sparingly in alcohol, but more readily in hot glacial acetic acid, from which it crystallises in hard, thick forms. When heated above its melting point, it becomes slightly coloured, and at about 200—220° evolution of hydrogen chloride commences. It is readily converted into tetrachloroketonaphthalene, and yields, therefore, with various reagents the same products as the two tetrachloroketones. Stannous chloride transforms it into trichloroketone, which on further reduction gives α-β-dichlor-α-naphthol. Alkaline sulphites, in acetic acid solution, and phenylhydrazine, convert it into trichlor-α-naphthol; potassium iodide acts similarly, tetrachloroketone being first formed. By continued boiling with alcohol, it yields small quantities of tetrachloroketonaphthalene, part of which is further transformed into dichlor-α-naphthaquinone. This last-named compound is obtained almost quantitatively on heating the pentachloride in sealed tubes at 120—130° with dilute alcohol or dilute acetic acid. When the pentachloride is treated with alkalis, the products, which vary according to the conditions of the experiment, are the same as those produced from tetrachloroketonaphthalene.

β-β-Chloranilidonaphthaquinone anilide, $C_6H_4<\begin{matrix}CO\cdot C(NHPh)\\ -C(NPh)\cdot CCl\end{matrix}>$, is formed when aniline is added to an alcoholic solution of the pentachloroketone; it crystallises from benzene in dark-red, shining needles, which melt at 157°, and are only sparingly soluble in alcohol and glacial acetic acid. The salts of this base are bluish-black, and are readily decomposed by alcohol or water. The *platinochloride*, $(C_{22}H_{15}ClN_2O)_2,H_2PtCl_6$, crystallises in small black-violet leaves with a metallic lustre. The anilide yields chloranilidonaphthaquinone when boiled with alcoholic hydrochloric acid.

Hexachloroketohydronaphthalene,  $C_6H_4<\begin{matrix}-CO\cdot CCl_2\\ CCl_2\cdot CCl_2\end{matrix}>$, is obtained by heating the tetrachloride with manganese dioxide and hydrochloric acid; when crystallised slowly from glacial acetic acid, it forms thick, hard, seemingly monoclinic forms, but when crystallisation proceeds slowly, long striated needles are obtained. It is readily soluble in benzene and hot alcohol, sparingly soluble in ether, and melts at 130°; when heated above this temperature, it loses chlorine. This compound is tolerably stable, it liberates iodine from potassium iodide only slowly, and does not react with aniline; it is converted into trichlor-α-naphthol by the action of reducing agents. When treated with alkalis in alcoholic solution, the ring is split, and an acid, $COOH\cdot C_6H_4\cdot CO\cdot CCl\colon CCl_2$, is obtained, which is identical with that produced from tetrachlorodiketonaphthalene (this vol., p. 490). This acid crystallises from dilute alcohol, or dilute acetic acid, in colourless, acute-angled rhombohedra, or in leaves which melt at 127—128°. When heated with concentrated sulphuric acid, it loses hydrochloric acid, and is converted into a compound which is probably a substituted hydrindenecarboxylic acid. F. S. K.

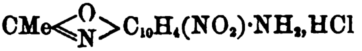
β-Tetrahydronaphthylamine. By E. BAMBERGER and R. MÜLLER (*Ber.*, **21**, 1112—1125; compare this vol., pp. 159, 599).—In its behaviour towards diazobenzene chloride, β-tetrahydronaphthylamine resembles the non-aromatic amines, and yields a *diazoamido*-derivative, $C_{10}H_{11}\cdot NH\cdot N_2Ph$, which combines with picric acid in ethereal solution to form a *picrate* crystallising in lustrous, ruby-red needles and melting at 118°. Diazoamidotetrahydro-β-naphthylamine is explosive, is volatile with steam, and when heated with dilute acids is decomposed for the most part into nitrogen, aniline, and dihydronaphthalene, a small quantity of β-tetrahydronaphthylamine and, probably, phenol being also formed. The tetrahydro-base is not attacked when boiled even for a day with hydrobromic acid (containing 47·8 per cent. of hydrogen bromide), but when heated with the acid at 150—160° is slowly decomposed into naphthalene, ammonia, and hydrogen; a similar result is also obtained by heating the base in sealed tubes at 80—100° above its boiling point for several days. The nitrite does not decompose below 160°, but when heated at 180—190° is converted into nitrogen, water, and dihydronaphthalene, together with some ammonia formed by a secondary reaction. The aqueous solution of a mixture of the tetrahydro-base and nitrous acid in molecular proportion is not affected by prolonged boiling, and only suffers decomposition to a slight extent when heated at 120—130° for 20 hours, naphthalene being formed; the solution of a similar mixture in dilute sulphuric acid (1 : 10) is, however, less stable, and decomposes on warming with the production of naphthalene and a small quantity of an oil. The formation of naphthalene, taken in conjunction with the fact that a certain proportion of the tetrahydro-base remains unchanged in these decompositions, renders it probable that the reaction proceeds normally with the formation of nitrogen, water, and a hydronaphthol, which then decomposes into water and dihydronaphthalene, the latter being finally oxidised to naphthalene at the expense of a portion of the nitrous acid. To avoid if possible this secondary reaction, amyl nitrite was employed as the diazotising agent instead of nitrous acid, with the result that dihydronaphthalene, amyl alcohol, nitrogen, and water were obtained.

Acetyltetrahydro-β-naphthylamine does not react with bromine in chloroform solution at 0°, from which the authors conclude that one of the two benzene nuclei is completely hydrogenated. To determine which, the tetrahydro-base was oxidised by suspending 3 grams in 250 c.c. of water containing a small quantity of sodium carbonate in solution, cooling to 10—12°, and adding in small quantities at a time 9 to 10 grams of a 4 per cent. permanganate solution; much ammonia escaped, and phthalic acid, together with Gabriel and Michael's hydrocinnamorthocarboxylic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COOH$ (Abstr., 1878, 426; this vol., p. 150), which constitutes the chief product under these conditions, were obtained, hence β-tetrahydronaphthylamine has the constitution $[H_2 : H_2 : H,NH_2 : H_2 = 1 : 2 : 3 : 4]$.

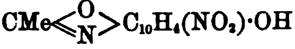
Valeryl-β-naphthylamine, $C_{10}H_7\cdot NH\cdot CO\cdot C_4H_9$, is formed in small quantity by the action of sodium on a boiling solution of β-naphthylamine in valeric acid; it crystallises in long, vitreous prisms, and melts at 138·5°. W. P. W.

Derivatives of Diamido-α-naphthol. By S. Meerson (*Ber.*, **21**, 1195—1199).—*Diamido-α-naphthol hydrochloride*, $OH\cdot C_{10}H_5(NH_2,HCl)_2$, can be prepared from the stannochloride obtained when Martius' yellow is reduced with tin and hydrochloric acid, by suspending it in water, precipitating the tin with hydrogen sulphide, evaporating the filtrate in a vacuum, and treating the residue with concentrated hydrochloric acid. It crystallises in colourless, microscopic tables, and is fairly stable in the dry state. When treated with anhydrous sodium acetate and acetic anhydride, it is converted into *triacetyldiamido-α-naphthol*, $C_{10}H_5(OAc)(NHAc)_2$, which crystallises from acetic acid in white, microscopic needles, melts at 280° with decomposition, and is insoluble in water, sparingly soluble in boiling alcohol. It dissolves also in dilute aqueous potash with a red colour, and is oxidised to *acetamidonaphthaquinone*, $C_{10}H_5O_2\cdot NHAc$, when the solution is acidified with hydrochloric acid and treated with ferric chloride. The quinone crystallises from alcohol in lustrous, golden-yellow scales, and melts at 198° with decomposition.

Nitrotriacetyldiamido-α-naphthol, $NO_2\cdot C_{10}H_4(OAc)\cdot(NHAc)_2$, is obtained when triacetyldiamido-α-naphthol suspended in acetic acid is treated in the cold with nitric acid (sp. gr. = 1·48) until solution occurs. It is a yellow, granular powder, melts at 235° with decomposition, and on oxidation with potassium permanganate yields phthalic acid. Fuming hydrochloric acid dissolves it on warming with the formation of *nitrodiamidoethenyl-α-naphthol hydrochloride*,


$CMe{<}\genfrac{}{}{0pt}{}{O}{N}{>}C_{10}H_4(NO_2)\cdot NH_2,HCl$ $[O : N : NO_2 : NH_2 = 1 : 2 : 3 : 4]$,

which crystallises in long, slender, lustrous, citron-yellow needles, and yields a *platinochloride*, $(C_{12}H_9N_3O_3)_2,H_2PtCl_6$, crystallising in dark-yellow needles. On treatment with water, the hydrochloride decomposes, yielding the *base*, which has a beautiful scarlet colour, and is only sparingly soluble in alcohol; by boiling with very dilute aqueous potash, it is converted into *hydroxynitroethenylamido-α-naphthol*,


$CMe{<}\genfrac{}{}{0pt}{}{O}{N}{>}C_{10}H_4(NO_2)\cdot OH$; this crystallises in slender, brown needles, and melts at 163° with decomposition.

Acetamidonaphthaquinoneacetimide, $NAc\cdot C_{10}H_5O\cdot NHAc$, is prepared by the action of anhydrous sodium acetate and acetic anhydride on diimido-α-naphthol hydrochloride. It crystallises from alcohol in thick, dark-yellow prisms, and melts at 178° with decomposition. On oxidation with nitric acid (sp. gr. = 1·48), it yields the acetamidonaphthaquinone already described, and on treatment with bromine (1 mol.) in acetic acid solution is converted into *bromacetamidonaphthaquinone*, $C_{10}H_4O_2Br\cdot NHAc$, which crystallises from alcohol in lustrous, golden-yellow needles, and melts at 205° with decomposition.

W. P. W.

Action of Phosphorus Pentachloride on α-Hydroxynaphthoïc Acid. By R. WOLFFENSTEIN (*Ber.*, **21**, 1186—1192; compare Abstr., 1887, 963).—*α-Carboxylnaphthylphosphoric acid*,

$$PO(OH)_2·O·C_{10}H_6·COOH,$$

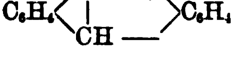
is prepared either by heating α-chlorocarboxylnaphthylorthophosphoric dichloride at 90° for several days until the weight is constant, or by allowing it to remain in contact with water for three weeks. It crystallises in slender, white needles, is readily soluble in acetone, less soluble in benzene, and though stable when dry, decomposes readily in aqueous solution into α-hydroxynaphthoïc acid and phosphoric acid. The *silver* salt, $C_{11}H_6PO_6Ag_3$, and *lead* salt, $(C_{11}H_6PO_6)_2Pb_3$, were prepared; the ammonium salt decomposes in aqueous solution into ammonium α-hydroxynaphthoate. The action of hot acetic acid on the dichloride resembles that of water, since α-carboxylnaphthylphosphoric acid is first formed, and this on further heating with the acid is converted into α-hydroxynaphthoïc acid and phosphoric acid.

α-Chlorocarboxylnaphthylorthophosphoric dichloride when treated with absolute alcohol (5 mols.) in the cold, yields a *diethyl* salt, $PO(OEt)_2·O·C_{10}H_6·CCl_3$, which is crystalline, melts at 63°, and decomposes when boiled with water. Phosphorus pentachloride reacts with the dichloride under pressure at 180°, forming *α-chloronaphthoïc trichloride*, $C_{10}H_6Cl·CCl_3$. This crystallises in colourless rhombohedra, melts at 73°, dissolves readily in the ordinary solvents, and gives the malachite-green reaction on boiling with dimethylaniline and zinc chloride. When boiled with water and acetic acid, it is converted into a *chloronaphthoïc acid*, $C_{10}H_6Cl·COOH$ [probably Cl : COOH = 1 : 2], which crystallises from benzene in slender, white needles, melts at 196°, and yields β-naphthoïc acid on treatment with sodium amalgam. The *silver* salt, $C_{10}H_6Cl·COOAg$, and *calcium* salt, $(C_{10}H_6Cl·CO_2)_2Ca + 2H_2O$, of this acid were prepared.

W. P. W.

Anthranol. By F. GOLDMANN (*Ber.*, **21**, 1176—1182).—Anthraquinone dichloride is obtained when a chloroform solution of anthranol is treated with dry chlorine. It crystallises in thin, pale-yellow monoclinic prisms, $a : b : c = 0·7973 : 1 : 0·6262$; $\beta = 72° 48'$; faces observed, ∞P, $0P$, and $-P$; it melts at 132—134°, and is identical with Thörner and Zincke's compound (Abstr., 1878, 231). Anthraquinone dibromide (Abstr., 1887, 1049) crystallises in pale-yellow, monoclinic forms, $a : b : c = 1·5009 : 1 : 1·4708$; $\beta = 70° 43'$; faces observed, $0P$, $-P$, $+P$, $\frac{1}{2}\bar{P}\infty$, and $+2\bar{P}2$.

When finely powdered anthranol (15 grams) dissolved as far as possible in boiling aqueous potash (15 grams) is heated with an excess of ethyl iodide (40 grams) in a reflux apparatus for 10 to 12 hours, an oil is obtained consisting of anthranyl ethyl ether and diethylanthrone; these can readily be separated, as the former is dissolved whilst the latter is precipitated in a crystalline form when the product is treated with light petroleum.



Anthranyl ethyl ether, $C_6H_4\left\langle\begin{array}{c}C(OEt)\\|\\CH\end{array}\right\rangle C_6H_4$, is a heavy, yellow oil, and dissolves readily in benzene, light petroleum, ether, alcohol, and acetic acid, yielding solutions showing a blue fluorescence. It could not be crystallised. On oxidation with chromic acid in acetic acid, it yields anthraquinone, and when dissolved in carbon bisulphide cooled at 15—20° and treated with bromine, it is converted into a yellow or red crystalline product which decomposes at the ordinary temperature into hydrogen bromide and *dibromanthranyl ethyl ether*,

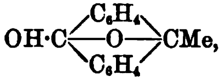
$$C_{14}H_7Br_2{\cdot}OEt.$$

This forms small, colourless crystals, melts at 116—117°, decomposes with the evolution of bromine and hydrogen bromide on further heating, and is soluble in benzene. On oxidation with chromic acid in acetic acid solution, it yields a derivative, $C_{16}H_{13}O_2Br$, which crystallises from benzene and light petroleum in large needles, and melts at 135—138°; further oxidation converts it seemingly into bromanthraquinone.

Diethylanthrone, $C_6H_4{<}{CEt_2 \atop CO-}{>}C_6H_4$, crystallises in colourless forms, melts at 136°, and is readily soluble in benzene, chloroform, alcohol, and ether, soluble in light petroleum, and insoluble in aqueous alkalis. It is slowly oxidised to anthraquinone by chromic acid in acetic acid solution, does not react with bromine in carbon bisulphide solution, and is not affected by heating at 180° with a solution of hydrogen chloride in acetic acid. When heated with hydriodic acid (sp. gr. = 1·7) and amorphous phosphorus at 180—200° for three hours, it is reduced to *diethylhydroanthracene*, $C_6H_4{<}{CEt_2 \atop CH_2}{>}C_6H_4$, which crystallises in colourless forms, melts at 48—50°, dissolves readily in light petroleum, benzene, ether, and carbon bisulphide, and is oxidised to diethylanthrone by chromic acid in acetic acid solution.

W. P. W.

Methyloxyanthranol. By C. LIEBERMANN (*Ber.*, **21**, 1175).—The author has again obtained the isomeric methyloxyanthranol,



$$OH{\cdot}C\left\langle\begin{matrix}C_6H_4\\ -O-\\ C_6H_4\end{matrix}\right\rangle CMe,$$

(Abstr., 1881, 608), together with the ordinary form, in one experiment in which oxyanthranol was allowed to remain with aqueous soda and methyl iodide in a pressure flask for a week, and then heated for a day at a temperature gradually rising to 70°; but all experiments to determine the conditions of its formation have failed, since only traces, at the most, of the compound have been subsequently obtained. The colourless needles of the isomeride, which were separated mechanically from the yellow scales of methyloxyanthranol, melted at 98°, and were extremely soluble in benzene and light petroleum.

W. P. W.

Ethylated Hydroxyanthraquinones. By C. LIEBERMANN and G. JELLINEK (*Ber.*, **21**, 1164—1171).—Liebermann and v. Kostanecki have stated that only those ethylated hydroxyanthraquinones which contain two free hydroxyl-groups in the alizarin position can be mordanted on fabrics (*Annalen*, **240**, 245). In order to obtain evidence confirmatory of this theory, the authors have ethylated five of the hydroxyanthraquinones. It was not found possible to prepare triethylated derivatives of anthrapurpurin, flavopurpurin, or anthragallol, although mono- and di-ethylated derivatives were readily obtained. In general it was found that ethylation proceeded the more rapidly the greater the number of hydroxyl-groups present, and the more these were grouped in contiguous positions in the formulæ of the compounds; moreover, with hydroxyanthraquinones containing three hydroxyl-groups in contiguous positions in their formulæ, it was found that the hydroxyl-group in the intermediate position was always ethylated first, although experiments with quinizarin and β-hydroxyanthraquinone showed that there was no perceptible difference in the ease with which hydroxyl-groups respectively in the α- and β- positions were displaced by ethoxyl. Spectroscopic observations showed that in solution in concentrated sulphuric acid, ethylated derivatives gave spectra closely resembling, and in some cases identical with those of the corresponding hydroxyanthraquinones.

Ethylation was effected in two ways, either by heating the hydroxyanthraquinone at 80° for some days in a reflux apparatus with dilute aqueous potash and an excess of ethyl iodide, or by heating the finely powdered hydroxyanthraquinone lead salt, dried at 120°, with a mixture of anhydrous benzene and ethyl iodide at 220° for 16 hours; the products obtained by the two methods were not always identical. The ethylated derivatives are very stable, and are not affected by boiling with ammonia, alkalis, or the ordinary solvents.

Ethoxyanthraquinone, $C_{14}H_7O_2\cdot OEt$, forms yellowish-white needles.

Quinizarin ethyl ether, $OEt\cdot C_{14}H_6O_2\cdot OH$, crystallises from alcohol in beautiful carmine needles, melts at 150—151°, forms a soluble barium salt, and is sparingly soluble in alkalis, yielding a red solution. The rose-red solution in sulphuric acid is fluorescent, as are the corresponding solutions of quinizarin and its diethyl ether; moreover, in passing from the former to the latter the colour of the solutions becomes more blue, just as is the case with eosin and its ethyl ether. *Quinizarin diethyl ether*, $C_{14}H_6O_2(OEt)_2$, crystallises in yellow needles and melts at 176—177°.

Anthragallol ethyl ether, $C_{14}H_5O_2(OH)_2\cdot OEt$ [$OEt = 2$], prepared by the first method, crystallises from alcohol in small, red needles, melts at 175°, is soluble in hot alcohol, benzene, ether, and acetic acid, dissolves in concentrated sulphuric acid with an orange-yellow colour, and has no tinctorial powers. The *diethyl ether*, $C_{14}H_5O_2(OEt)_2\cdot OH$, prepared by the first method, forms brown needles, melts at 134°, dissolves in concentrated sulphuric acid with an orange colour, and has no tinctorial powers. Prepared by the second method, *anthragallol ethyl ether* crystallises from alcohol in small, red needles, melts at 245°, is sparingly soluble in ether and alcohol, and dissolves in alkalis with a blue colour, yielding solutions which, unlike those of anthragallol, are not oxidised on exposure to air. It dissolves in concentrated sulphuric acid with a reddish-brown colour, and dyes mordanted fabrics. The *diethyl ether* prepared by the second method crystallises from alcohol in silky, citron-yellow needles, melts at 198°, is readily soluble in ether and in hot alcohol, benzene, and acetic acid, dissolves in sulphuric acid with a reddish-yellow colour, and is destitute of tinctorial powers.

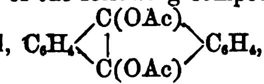
Anthrapurpurin ethyl ether, $C_{14}H_5O_2(OH)_2\cdot OEt$, prepared by the first method, crystallises from alcohol in vitreous, orange-red needles, melts at 265°, is soluble in ether, &c., and dissolves in concentrated sulphuric acid with a reddish-violet colour. The *diethyl ether*, $C_{14}H_5O_2(OEt)_2\cdot OH$, crystallises in matted, yellow needles, melts at 162°, is soluble in ether, &c., and dissolves in concentrated sulphuric acid with a reddish-violet colour. The *ethyl ether*, obtained as sole product by the second method, is deemed identical with that just described, although it crystallises in bright-yellow needles, melts at 170°, and gives a reddish-violet colour with concentrated sulphuric acid. These derivatives are destitute of tinctorial powers.

Flavopurpurin ethyl ether, $C_{14}H_5O_2(OH)_2\cdot OEt$, is obtained in very small quantity by the first method, and is readily soluble in ether and alcohol. The *diethyl ether*, $C_{14}H_5O_2(OEt)_2\cdot OH$, crystallises from dilute alcohol in long, hair-like, reddish-yellow needles, melts at 209°, is sparingly soluble in ether and alcohol, readily soluble in hot acetic acid, and dissolves in concentrated sulphuric acid with a blood-red colour. This derivative is the sole product obtained by the second method. These compounds have no tinctorial powers.

Rufigallol ethyl ether, $C_{14}H_2O_2(OH)_3(OEt)_3$, prepared by the first method, crystallises in long, orange-red needles, melts at 195°, is sparingly soluble in alcohol, dissolves in concentrated sulphuric acid with a violet colour, and is destitute of tinctorial powers.

W. P. W.

Leuco-compounds from Anthraquinone Dyes. By C. LIEBERMANN (*Ber.*, **21**, 1172—1174; compare this vol., p. 492).—The method of simultaneously reducing and acetylating anthraquinone-derivatives by means of zinc-dust, sodium acetate, and acetic anhydride has been employed in the preparation of the following compounds:—

Diacetylhydroxyanthranol,  $C_6H_4\left\langle\begin{matrix}C(OAc)\\|\\C(OAc)\end{matrix}\right\rangle C_6H_4$, obtained by the reduction of anthraquinone, crystallises from acetic acid in colourless needles, melts at 260° with decomposition, and is identical with the compound prepared by acetylating hydroxyanthranol (Abstr., 1882, 855).

Diacetylmethylhydroxyanthranol, $C_6H_4:C_2(OAc)_2:C_6H_3Me$, prepared by the reduction of methylanthracene (m. p. = 177°), crystallises in scales melting at 217°.

Pentacetylhydroxyanthranol, $C_6H_4:C_2(OAc)_2:C_6H(OAc)_3$, formed by the reduction of anthragallol, crystallises from dilute alcohol in needles, and melts at 203°.

Tetracetylhydroxyanthranol, $OAc\cdot C_6H_3:C_2(OAc)_2:C_6H_3\cdot OAc$, is obtained, together with a compound which is soluble in 50 per cent. alcohol, by the reduction of anthraflavic acid, and crystallises from acetic acid in silky needles melting at 274°.

Tetracetylhydroxyanthranol, $OAc\cdot C_6H_3:C_2(OAc)_2:C_6H_3\cdot OAc$, forms one of two compounds obtained by the reduction of isoanthraflavic acid, and is separated by means of its sparing solubility in 50 per cent. acetic acid. It crystallises from alcohol in needles melting at 235—240°.

The more soluble products, which are simultaneously formed during the reduction-acetylation process, seem to be the corresponding peracetylated anthranols, and the yield of these is increased by increasing the duration of the reaction. Thus, flavopurpurin (this vol., p. 493) forms a pentacetylhydroxyanthranol as the chief product under the ordinary conditions, but when the reduction is continued for some time the proportions are reversed, and the tetracetylanthranol becomes the chief product. The tetracetyl-derivative melts not at 103—105°, but at 250—260°. W. P. W.

Additive Derivatives of Dianthryl. By H. SACHSE (*Ber.*, **21**, 1183—1185).—*Dichlorodianthryl octochloride*, $C_{28}H_{16}Cl_2,Cl_8$, is obtained, together with a small quantity of dichloranthracene tetrachloride by treating a solution of dianthryl in chloroform with the calculated quantity of chlorine. It crystallises in white, microscopic scales, and is readily soluble in chloroform, benzene, and ether, and sparingly soluble in alcohol, acetic acid, and light petroleum, yielding nonfluorescent solutions which become fluorescent on heating owing to the decomposition of the compound. At 80°, it decomposes without previous fusion with the evolution of hydrogen chloride, and when heated with alcoholic potash for 1 to 2 hours is converted into *hexachlorodianthryl*, $C_{28}H_{12}Cl_6$. This crystallises in microscopic, greenish-yellow prisms, melts at 308—310°, and is readily soluble in benzene, sparingly soluble in alcohol and acetic acid, yielding fluorescent solutions.

Dibromodianthryl octobromide, $C_{28}H_{16}Br_2,Br_8$, is formed, together with a small quantity of dibromanthracene tetrabromide, when dianthryl is carefully treated with bromine in the cold. It crystallises in microscopic scales, melts at 156—160° with the evolution of bromine, is more stable than the octochloride, and dissolves readily in benzene and ether, but sparingly in alcohol and acetic acid, forming non-fluorescent solutions. When heated with alcoholic potash, a substitution-derivative, probably hexabromodianthryl, is obtained which crystallises in dark yellow prisms, melts at above 300°, and dissolves in acetic acid, yielding a fluorescent solution. W. P. W.

Action of Acetic Acid on Citrene. By J. LAFONT (*J. Pharm.* [5], **17**, 105—108, 185—188).—Essence of citron, on fractional distillation, yields citrene, $C_{10}H_{16}$, as a principal product; this boils at about 178°, and has a rotatory power of $[\alpha]_D = +93°$. When mixed with 1½ vols. of glacial acetic acid, and heated on the water-bath for 48 hours out of contact with air, it is partly converted into an acetate, $C_{10}H_{16},C_2H_4O_2$, which distils in a vacuum at 140—143°, has a sp. gr. of 0·9828 at 0°, and a rotatory power of $[\alpha]_D = +52° 30'$; when saponified with alcoholic potash at 100°, a heavy viscous liquid, $C_{10}H_{16},H_2O$, is obtained which distils at 126—128°, under a pressure of

40 mm., and has the distinct odour of hyacinth shown by List's terpilenol. Its rotatory power is $[\alpha]_D = +67° 30'$.

Citrene, when treated with formic acid in the cold during three months, affords some cymene and a compound, $C_{20}H_{32}$, which boils at 212°. This is a viscous, yellow substance with odour resembling that of copaiba, sp. gr. = 0·9404 at 0°; it does not affect polarised light. Citrene and formic acid give the same products when heated at 100° in a sealed tube during 18 hours. J. T.

Terpinol. By G. BOUCHARDAT and R. VOIRY (*Compt. rend.*, **106**, 663—665).—When terpilenol, boiling at 172—176° (Abstr., 1887, 677), is saturated with hydrogen chloride at −25°, the oxygen compound, for which the authors propose the name *terpane*, is converted into the hydrochloride $2C_{10}H_{18}O,HCl$, whilst the terpilenic hydrocarbon forms the hydrochloride $C_{10}H_{16},2HCl$. If the liquid is not cooled, the terpane is at once converted into the dihydrochloride. When the compound $(C_{10}H_{18}O)_2,HCl$ is washed with water at 0°, it is decomposed with development of heat and liberation of terpane. The hydrochloric acid is removed by treatment with dilute alkali, and the terpane is distilled under a pressure of 15 mm. at a temperature not exceeding 80°. The product boils at 78—79° in a vacuum, and is impure, but yields solid terpane if cooled to −50—55°; the formation of crystals being accelerated by the addition of a fragment of the terpane from eucalyptol. This terpane boils at 174°, and its sp. gr. (0·935 at 0°) and melting point (−3° to −1°) are identical with those of terpane from eucalyptol and similar natural products. Its odour recalls that of menthol, &c. Hydrogen chloride converts it into the crystalline hydrochloride, $(C_{10}H_{18}O)_2HCl$, which liquefies in a vacuum or under water with liberation of terpane. In a sealed tube, it decomposes spontaneously into $C_{10}H_{16},2HCl$, $C_{18}H_{18}O$ and water. When treated with an ethereal solution of bromine, terpane yields a granular cinnabar-red product, which is a mixture of a red additive product with colourless substitution-derivatives; this reaction, like that with hydrochloric acid, may be used to separate terpane from terpilenol but requires greater precautions. The terpane thus obtained always retains a small quantity of a hydrobromide of sp.-gr. above 0·977, analogous to but more stable than the hydrochloride.

It follows from these reactions that List's terpilenol consists of inactive crystalline terpinol or terpol, $C_{10}H_{18}O$, boiling at 218°; terpane, $C_{10}H_{18}O$, boiling at 175° and crystallising at −1°; and inactive terpilene, $C_{10}H_{16}$.

Terpane differs from active and inactive terpilenols in that it does not combine with acids or anhydrides to form ethereal salts. This confirms Wallach's observations, and supports his view that terpane is the ether or anhydride of terpene. C. H. B.

Oxidation of Hydrazocamphenes. By C. TANRET (*Compt. rend.*, **106**, 660—662 and 749—751).—If a cold solution of α-hydrazocamphene in 1 per cent. sulphuric acid is gradually mixed with standard potassium permanganate solution until the colour just ceases to be discharged, it yields a blue precipitate of *azocamphene*,

$C_{40}H_{64}N_4O_8$. This is dissolved in ether, and the solution first washed with water and with dilute soda solution and then evaporated to dryness. Azocamphene thus obtained melts at 153°, and is insoluble in water but very soluble in cold ether, alcohol, and chloroform. A 50 per cent. ethereal solution gradually deposits a white crystalline powder which is insoluble in cold alcohol or ether but dissolves on heating with formation of a blue solution. The crystals become blue at 80°, and if kept at this temperature for some time regain their solubility in cold alcohol or ether. The white crystals have the same composition as the blue compound, melt at 153°, and are insoluble in cold water but dissolve in their own weight of chloroform, the solution becoming blue. It is evident that azocamphene can exist in two modifications, which the author distinguishes as *cyanazocamphene* and *leucazocamphene*. The azocamphene from β-hydrazocamphene exists only in the form of a blue resinous mass. Azocamphene is neutral to litmus and does not give with ferric chloride the violet coloration characteristic of the hydrazocamphenes.

At a temperature somewhat above its melting point, azocamphene decomposes with evolution of oxides of nitrogen. It also decomposes when heated with dilute acids or even with water, yielding hydrazocamphene and an acid, $C_{20}H_{32}N_2O_5$, which is somewhat resinous and is only slightly soluble in water, but dissolves in ether or chloroform. Its salts with alkalis and alkaline earths are soluble in water; the silver salt is only slightly soluble. Prolonged boiling with water decomposes it with production of a new acid which is insoluble in ether and has a high rotatory power.

Concentrated nitric acid acts very violently on the hydrazocamphenes, but the diluted acid yields the blue azocamphene, which, however, rapidly disappears. When the reaction has moderated, strong nitric acid is added, and the product is crystallised by concentration and converted into the calcium salt, which is recrystallised and then decomposed by hydrochloric acid. The *terebenthic acid*, $C_8H_{12}O_5$, thus obtained forms small anhydrous rhomboidal prisms, soluble in 8·2 parts of water at 14° and in 23 parts of ether, very soluble in alcohol, but insoluble in chloroform. It is optically inactive, melts at 164°, and at a higher temperature loses water, and then partially decomposes. When small quantities are distilled, a syrupy anhydride, soluble in chloroform, is obtained. When fused with potash, it decomposes above 240° with evolution of hydrogen and production of acetate, oxalate, and formate.

Terebenthic acid is bibasic, and the normal salts of the alkalis and alkaline earths are soluble and non-crystallisable. The acid ammonium salt forms slender needles soluble in eight parts of water. The acid calcium salt is only very slightly soluble and forms microscopic crystals. Neutral solutions of terebenthates give precipitates with solutions of silver, copper, lead, and iron (ferric), but no precipitates with solutions of zinc, cobalt, nickel, manganese, or mercury. The silver salt is granular, the copper salt is a blue-green powder. The normal zinc salt is soluble and non-crystallisable; when heated with water at 45°, it decomposes into a soluble acid salt, and a basic salt which is insoluble in the hot liquid but is partially decomposed when the liquid cools, and yields a solution which, if concentrated, coagulates at 24°, but becomes limpid again when cooled.

Terebenthic acid is obtained from both α- and β-hydrazocamphene. Nitric acid also produces other acids less rich in carbon and not crystallisable.

Monohydrated sulphuric acid has no action on the hydrazocamphenes in the cold, but if the hydrazocamphene is treated at 200° with one-fifth its weight of acid it blackens, swells up, and evolves nitrogen and sulphurous anhydride. When the residue is treated with water and agitated with chloroform, it yields dihydrocamphines, $C_{20}H_{34}N_2O_4$, which are also formed, together with an alkaline carbonate and cyanide, when hydrazocamphenes are fused with potash.

Chromic acid converts hydrazocamphenes into neutral brown resinous products, insoluble in water, but soluble in alcohol, ether, and chloroform. C. H. B.

Diterebenthyl. By A. RENARD (*Compt. rend.*, **106**, 856—858).—Diterebenthyl was allowed to fall drop by drop into an iron tube heated to incipient redness. Very little carbon was deposited, but some hydrogen, mixed with ethylene and propylene, was given off. The fraction of the product boiling below 70° contained amylene and hexylene, pentane, and hexane. The fraction at 70—78° contains hexine, and that at 100—110° consists chiefly of heptine. The most abundant fraction boils at 150—180°, and contains cymene and terebenthene hydrocarbons. It is evident that when decomposed by heat diterebenthyl yields practically the same product as terebenthene or essence of resin obtained by the distillation of colophony.

Bromine in carbon bisulphide forms the unstable derivative $C_{20}H_{30}Br_2$, which, when heated at 300°, yields diterebenthylene, a colourless, slightly fluorescent, thick oily liquid which boils at 345—350°; sp. gr. at 12° = 0·9821; rotatory power for D in a column 1 cm. long = +4°; vapour-density, 9·3. It does not alter when exposed to air, and is not affected by hydrogen chloride. Bromine yields the compound $C_{20}H_{24}Br_4$ as a deep-brown, amorphous mass. Well-cooled fuming nitric acid dissolves the hydrocarbon without evolution of nitrogen oxides, and on adding water the trinitro-derivative, $C_{20}H_{25}(NO_2)_3$, separates as a bulky, flocculent, yellow precipitate. Cold concentrated sulphuric acid has no action, but the hot acid or, better, the fuming acid, yields a sulphonic acid, $C_{20}H_{27}\cdot SO_3H$, distinguished from diterebenthylsulphonic acid by its greater mobility. C. H. B.

Camphor Bases. By E. BAMBERGER (*Ber.*, **21**, 1125—1131).—In a previous paper the author has called attention to the analogy existing between the bases of the camphor-group and β-tetrahydronaphthylamine (this vol., p. 159). This is well shown in the case of bornylamine, which, like β-tetrahydronaphthylamine, has a peculiar piperidine-like odour, is strongly alkaline, and reacts with diazobenzene chloride to yield an oil having properties similar to those of diazoamidotetrahydro-β-naphthylamine (compare this vol., p. 712). Bornylamine nitrate is not decomposed by prolonged boiling with water, and noteworthy quantities escape decomposition when a 10 per cent. aqueous solution is heated at 130° for four hours. Finally, just as β-tetrahydronaphthylamine decomposes into naphthalene, ammonia, and hydrogen (*loc. cit.*), so bornylamine seems to yield ammonia and either camphor or its decomposition products. On these grounds, the author considers that bornylamine is a tetrahydro-derivative of an aromatic base, and is probably tetrahydrocarvacrylamine. From this it follows that camphor, which yields bornylamine on treatment with ammonium formate (Leuckart and Bach, Abstr., 1887, 376), a reaction involving, as Leuckart has shown, the displacement of the oxygen present in the carbonyl-group by hydrogen and the amido-group, is a ketotetrahydrocymene [Pr : O : Me = 1 : 3 : 4].

Camphylamine, which Leuckart (*loc. cit.*) regards as a position-isomeride of bornylamine, differs from the latter, since it has the properties of a fatty amine, and yields a hydroxy-derivative in the usual way. The remainder of the paper is devoted to a discussion of the probable formulæ of the anhydride of camphoroxime.

W. P. W.

Lactucerin. By O. HESSE (*Annalen*, **244**, 268—273).—The melting point of pure α-lactucerol varies. If the temperature is slowly raised it melts at 173°, but if it is rapidly heated it melts at 181°. The *diacetate*, prepared by boiling a mixture of lactucerol with acetic anhydride, crystallises in plates and melts at 198—200°. The *monacetate* melts between 202° and 207°. The *dibenzoate* is freely soluble in ether, chloroform, and light petroleum. It melts at 156°.

W. C. W.

Apiole. By J. GINSBERG (*Ber.*, **21**, 1192—1194).—When apiole is boiled with alcoholic potash, a compound is obtained, which crystallises in satiny scales, and has the same percentage composition as apiole (compare v. Gerichten, this Journal, 1876, ii, 533). On oxidation with nitric acid (sp. gr. = 1·48), apiole yields oxalic acid and a *nitro*-compound. This crystallises in lustrous, golden needles, melts at 116°, and on reduction with stannous chloride and alcoholic hydrogen chloride is converted into a *base*, which crystallises from water in long, yellow needles, melts at 118°, dissolves in mineral acids with a red colour, and gives with ferric chloride a violet coloration rapidly changing to blood-red. The *picrate* of the base crystallises in small, brown scales; the *hydrochloride* is an indistinctly crystalline powder, and the *acetyl*-derivative crystallises in colourless scales, melts at 260°, and is sparingly soluble in cold alcohol and ether. W. P. W.

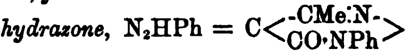
Emodin in Nephroma Lusitanica. By E. BACHMANN (*Chem. Centr.*, 1888, 47, from *Ber. deut. Bot. Ges.*, **5**, 192—194).—The colouring matter obtained from this lichen behaves towards alkalis like crysophanic acid, but differs from the latter in being readily soluble in alcohol, glacial acetic acid, and amyl alcohol. The colouring matter agrees most closely with emodin, a substance first found in rhubarb, and occurring also in the bark and berries of *Rhamnus frangula*.

J. P. L.

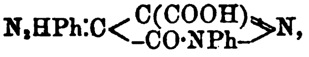
Chlorophyll. By J. Wollheim (*Ann. Agronom.*, **14**, 141—143, from *Bot. Centr.*, **32**, 310).—The author, who has been studying this substance both spectroscopically and chemically for some time past, gives the following preliminary notice of his results:—

The fresh solution in absolute alcohol is fluorescent, whilst the colouring matter in the fresh leaf is not. The absorption-bands are the same in relative intensity, but are narrower, and a little displaced towards the blue end of the spectrum. Fuming hydrochloric and sulphuric acids give non-fluorescent solutions with absorption-bands exactly like those of the fresh leaf. It is therefore evident that the colouring matter is changed by the action of alcohol. On adding water to the acid solutions, or weak acids to the alcoholic solution, a greenish-brown precipitate is obtained, soluble in alcohol, ether, chloroform, and benzene, giving the first two bands like the fresh tincture, the band III more feeble, IV stronger, and in addition a fifth band between $\lambda = 491$ and $\lambda = 509$, which has already been observed in the fresh leaf, but which appears to belong to a second absorbing substance. Fresh leaves treated with alkalis give fluorescent solutions with absorption-bands still more displaced towards the blue, and also the band III feebler and IV stronger than in the tincture. When the alkaline solution is gently heated, the bands are restored to their normal intensity, and the fluorescence disappears, but the displacement of the bands persists. When the greenish-brown precipitate (chlorophyllane) is dissolved in pure hydrochloric acid, the green solution (Frémy's phyllocyanin) again gives the spectrum of the fresh tincture. It seems, therefore, that certain atoms combined during the formation of chlorophyllane, and causing the reinforcement of band IV, are removed or substituted under the influence of hydrochloric acid. Water gives with this solution another precipitate (phyllocyanic acid), whose alcoholic solution shows a strong band IV. This suggests the entrance of hydroxyl into the combination. The spectrum of phyllocyanic acid is identical with that of chlorophyllane. The precipitate, redissolved and reprecipitated many times, washed, and taken up by chloroform, may be obtained in crystals; after many crystallisations these contain no iron or mineral matter, and give on analysis numbers corresponding with the formula $C_{28}H_{47}N_3O_6$. Phyllocyanic acid is a compound with a fatty substance. Its ammoniacal solution being precipitated with lead acetate, the precipitate extracted with alcohol, and the green alcoholic solution decomposed with hydrogen sulphide, the reddish-brown substance is left in the alcoholic solution, which is fluorescent, and gives the spectrum of chlorophyllane; whilst the band V has disappeared, showing that it belonged to the fatty substance precipitated by the lead salt. The fatty substance, whose spectrum coincides with that of xanthophyll, is no other than cholesterin. The red-brown substance thus freed from cholesterin is called by the author phyllorubin, and has the properties of an alcohol. On oxidation it behaves exactly like the bilirubin of the bile, becoming in succession blue, violet, red, and yellow. Oxidised with precaution, it yields an acid, whose copper salt shows the same displacement of absorption-bands towards the blue as alkaline chlorophyll. This copper salt is easily formed, and is the substance that gives the fine blue-green non-fluorescent colour to vegetable preparations made in copper vessels.

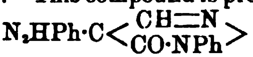
When phyllorubin is dissolved in chloroform and treated with a current of dry hydrogen chloride, phyllocyanin is first formed (giving the same spectrum as the alcoholic tincture of chlorophyll), and afterwards a greenish-blue colouring matter, the spectrum of which is identical with that of the fresh leaf. The same substance is formed by treating phyllorubin with other dehydrating reagents, such as sulphuric and phosphoric acids. It should therefore be considered as an ether (hydroxy-derivative?). It separates from the chloroform solution in crystalline plates with metallic lustre, and its behaviour with reagents is the same as that of chlorophyll. The chloroform solution is non-fluorescent, but either alcohol or glycerol gives a fluorescent solution with displaced spectrum. J. M. H. M.

Identity of Phenylmethylpyrazoloneazobenzene with Phenylhydrazineketophenylmethylpyrazolone: Inner Anhydride Formation of Diphenylhydrazineacetylglyoxylic Acid and Diphenylhydrazinedihydroxytartaric Acid. By L. KNORR (*Ber.*, **21**, 1201—1205).—Phenylmethylpyrazoloneazobenzene (Abstr., 1887, 602) is identical with phenylhydrazinephenylmethylketopyrazolone (*ibid.*, 603). Both compounds melt at 155°; they crystallise from hot alcohol in orange-red, shining needles, which dissolve in hot dilute soda, forming a deep yellow solution, from which they are precipitated in the form of the sodium salt by the addition of strong soda. When the alkaline solution of either compound is acidified, the original substance, melting at 155°, is obtained. On warming a nitric acid solution of either compound, the whole suddenly solidifies to a mass of fine, yellow needles. This new substance is *phenylmethylketopyrazolonehydrazone*,  $\mathrm{N_2HPh} = \mathrm{C}\Big<\genfrac{}{}{0pt}{}{\mathrm{-CMe{:}N-}}{\mathrm{CO{\cdot}NPh}}\Big>$. Its solubility in soda is probably owing to the formation of the sodium salt of diphenylhydrazineacetylglyoxylic acid, and on acidifying the free acid is converted into the inner anhydride. Similarly, on acidifying, an alkaline solution of the osazone of acetylglyoxylic acid (*loc. cit.*), the inner anhydride phenylhydrazinephenylmethylketopyrazolone is obtained.

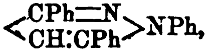
Diphenylhydrazinedehydroxytartaric acid (Ziegler and Locher, Abstr., 1887, 578) is converted into the inner anhydride when its alkaline solution is poured into acetic acid, or when the acid is crystallised from acetic acid. This anhydride,



$$\mathrm{N_2HPh{:}C}\Big<\genfrac{}{}{0pt}{}{\mathrm{C(COOH)}}{\mathrm{-CO{\cdot}NPh-}}\Big>\mathrm{N},$$

phenylhydrazineketophenylpyrazolonecarboxylic acid, melts at 230—232°, and loses 1 mol. of carbonic anhydride when carefully heated at 230°; a brown oil is thus obtained, which solidifies on cooling, and yields brown-yellow crystals, melting at 150° after recrystallisation from alcohol. This compound is probably phenylhydrazineketophenylpyrazolone,  $\mathrm{N_2HPh{\cdot}C}\Big<\genfrac{}{}{0pt}{}{\mathrm{CH{=}N}}{\mathrm{CO{\cdot}NPh}}\Big>$; on heating a few degrees above 230°, it is completely decomposed. The same substance appears to be formed by boiling the osazone of glyoxalcarboxylic acid (Nastvogel, *Inaug. Diss.*, Würzburg, 1887) with acetic anhydride. F. S. K.

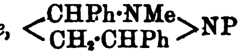
Pyrazoles and Pyrazolines. By L. Knorr and H. Laubmann (*Ber.*, **21**, 1205—1212).—1.3.5-*Triphenylpyrazole*,



$$<\begin{matrix}CPh{=}N\\CH{:}CPh\end{matrix}>NPh,$$

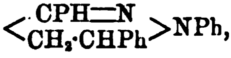
is obtained by warming dibenzoylmethane with an excess of phenylhydrazine. It crystallises from ether in large, well-defined plates, melting at 137—138°, and from dilute alcohol in leaflets which contain varying quantities of alcohol, according to the concentration of the solution, and yield the pure pyrazole when gently heated. It is insoluble in water and dilute acids, sparingly soluble in cold ether and alcohol, but dissolves readily in hot alcohol or ether, in chloroform, benzene, and glacial acetic acid. Triphenylpyrazole has only a feebly basic character, and is completely precipitated from its solution in concentrated sulphuric or nitric acid by the addition of water. It remains unchanged when heated with 20 per cent. hydrochloric acid at about 300°.

Triphenylpyrazole methiodide, $C_{22}H_{19}N_2I$, is formed when the pyrazole is heated with an excess of methyl iodide and methyl alcohol at 110°. It forms white needles, which melt at 176° with decomposition, and are sparingly soluble in cold, more readily in warm water. It dissolves in alcohol and chloroform, but is insoluble in alkalis, ether, and benzene. When heated, it yields methyl iodide and triphenylpyrazole.

Triphenylmethylpyrazine,  $<\begin{matrix}CHPh{\cdot}NMe\\CH_2{\cdot}CHPh\end{matrix}>NPh$, is produced by the action of sodium on a boiling alcoholic solution of the preceding compound. It melts at 109—110° or when placed in boiling water; it is insoluble in water, and only sparingly soluble in cold alcohol and light petroleum, but dissolves readily in hot alcohol, ether, and benzene, the solutions showing a slight blue fluorescence. This compound does not show the reactions of pyrazolines, and it yields a brown resinous product when treated with concentrated nitric acid.

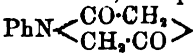
Bromotriphenylpyrazole, $C_{21}H_{15}N_2Br$, is obtained by treating a chloroform solution of the pyrazole with bromine. It crystallises from alcohol in white, shining, silky needles, which melt at 142°, and dissolve readily in ether, benzene, and hot alcohol, but are insoluble in water and dilute acids. It does not lose bromine when treated with aqueous or alcoholic potash.

Nitrosotriphenylpyrazole, $C_{21}H_{15}N_3O$, is formed when nitrous acid is passed into an ethereal solution of the pyrazole. It crystallises in green needles, which melt at 183°, are sparingly soluble in ether and light petroleum, but dissolve readily in benzene and chloroform. An aqueous or sulphuric acid solution of nitrous acid does not act on triphenylpyrazole.

1.3.5-*Triphenylpyrazoline*,  $<\begin{matrix}CPH{=}N\\CH_2{\cdot}CHPh\end{matrix}>NPh$, is obtained by reducing triphenylpyrazole with sodium and alcohol, or by warming an alcoholic solution of benzalacetophenone with phenylhydrazine. It crystallises in needles, melting at 134—135°, dissolves readily in ether, benzene, hot alcohol, and glacial acetic acid, with blue fluorescence, but is insoluble in water and dilute acids. It is only acted on at 300° by a 20 per cent. solution of hydrochloric acid, and a solution of this compound in sulphuric acid is turned blue-green by a drop of a nitrite solution. Triphenylpyrazole is formed when gaseous nitrous acid is passed into an ethereal solution of this compound until the blue fluorescence disappears; if the gas is passed for a longer time, the yellow solution becomes deep green, and nitrosotriphenylpyrazole (see above) is obtained; when, however, the triphenylpyrazoline is just covered with a small quantity of ether and nitrous acid passed, a brownish-yellow, indifferent substance is produced. This compound is insoluble in water, acids, and alkalis, and dissolves very sparingly in alcohol and ether; it is, however, readily soluble in chloroform and benzene, and crystallises from glacial acetic acid in forms melting at 175—176°. It appears to be *nitrotriphenylpyrazoline*, $C_{21}H_{17}N_3O_2$. The same compound, together with triphenylpyrazole, is produced when triphenylpyrazoline, in ethereal solution, is oxidised with nitric acid.

Triphenylpyrazoline tribromide, $C_{21}H_{18}N_2Br_3$, is obtained by treating a chloroform solution of triphenylpyrazoline with bromine. It crystallises from ether, alcohol, or light petroleum, in small needles, melting at 179°, and is reconverted into the pyrazoline by nascent hydrogen. F. S. K.

1.5-Diphenylpyrazoline. By H. LAUBMANN (*Ber.*, **21**, 1212—1213).—1.5-*Diphenylpyrazoline*, $C_{15}H_{14}N_2$, can be obtained by distilling the hydrazine of cinnamaldehyde (Fischer, Abstr., 1884, 1151). It crystallises from alcohol or light petroleum in shining, silky needles, melting at 137—138°. It is insoluble in water, sparingly soluble in light petroleum, dissolves more readily in alcohol, and readily in ether, benzene, and chloroform, the solutions showing a slight blue fluorescence. It gives a pyrazoline reaction similar to that shown by methyldiphenylpyrazoline (Knorr and Blank, Abstr., 1885, 506). Acid solutions of this compound are coloured magenta by oxidising agents. F. S. K.

Decomposition of Anilides at a High Temperature. By C. A. BISCHOFF (*Ber.*, **21**, 1257—1265; compare Abstr., 1883, 919).—*Diphenyldiketopiperazine*,  $PhN<\begin{matrix}CO\cdot CH_2\\CH_2\cdot CO\end{matrix}>NPh$, is obtained by the action of aniline on chloracetic acid or ethyl chloracetate.

Phenylglycinphenylamidacetic acid, $NHPh\cdot CH_2\cdot CO\cdot NPh\cdot CH_2\cdot COOH$, and *methylphenylglycinanilide*, $NHPh\cdot CH_2\cdot CO\cdot NPhMe$, are also produced by acting on chloracetic acid with aniline. The former compound is also formed when diphenyldiketopiperazine is boiled with strong acids or alkalis.

Paratoluidine chloracetate, $C_6H_4Me\cdot NH_2\cdot O\cdot CO\cdot CH_2Cl$, forms colourless crystals, which melt at 97·5° and are readily soluble in alcohol and ether.

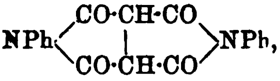
Paraditolyldiketopiperazine, $C_6H_4Me\cdot N<\substack{CO\cdot CH_2\\ CH_2\cdot CO}>NC_6H_4Me$, is produced when the preceding compound is heated; it can also be obtained from ethyl monochloracetate and *paratolylglycintoluide*,

$$C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4Me.$$

The last-named compound crystallises from hot alcohol in leafy forms which melt at 134°.

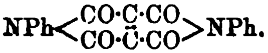
Orthotoluidine chloracetate, $C_9H_{12}NO_2Cl$, melts at 95°, dissolves readily in alcohol and warm water, less readily in ether.

Orthoditolyldiketopiperazine is obtained from toluidine and chloracetic acid or ethyl chloracetate. By heating aniline with malic acid, a compound, $PhN<\substack{CO\cdot CH{:}CH\cdot CO\\ CO\cdot CH{:}CH\cdot CO}>NPh$, is produced. Similarly ethyl acetylenetetracarboxylic acid yields a compound,



$$NPh<\substack{CO\cdot CH\cdot CO\\ |\\ CO\cdot CH\cdot CO}>NPh,$$

and ethyl dicarbintetracarboxylic acid gives a compound,



$$NPh<\substack{CO\cdot C\cdot CO\\ CO\cdot C\cdot CO}>NPh.$$

The above compounds will be more fully described in a future publication. F. S. K.

Pyridine Bases from Coal-tar. By J. MOHLER (*Ber.*, 21, 1006—1015).—The existence of a pyridine hydrate, $C_5NH_5,3H_2O$, seems to be confirmed by the author's experiments. β-Picoline was isolated from a mixture of coal-tar bases, and symmetrical collidine was obtained from the same source by fractional precipitation with potassium ferrocyanide.

Collidine from coal-tar is a colourless liquid which does not change on exposure to the air. It dissolves slowly but to a considerable extent in cold water, and separates again almost quantitatively on warming. The *mercurochloride*, $C_5H_2Me_3N,HCl,2HgCl_2$, crystallises in prisms melting at 155°, and is only sparingly soluble in water. The *aurochloride*, $C_8H_{11}N,HAuCl_4$, forms long, yellow needles which become brittle and dull on exposure to the air; the dry salt melts at 114—115°, but when heated under water it changes to an oil at a lower temperature. The *dichromate*, $(C_8H_{11}N)_2,H_2Cr_2O_7$, crystallises from water in long, yellow prisms which decompose at 190°, and are sensitive to light, becoming greyish-yellow coloured in the sunlight. The *picrate* crystallises in long, silky needles melting at 155—156°. The sulphate, nitrate, and hydrochloride are not deliquescent. The *hydrochloride* forms slender needles which sublime, with partial decomposition, without melting. The *sulphate* forms transparent prisms melting at 203°. The *nitrate* crystallises in hexagonal leaves which melt above 300° with decomposition.

Pyridine ferrocyanide, $(C_5H_5N)_2,H_4Fe(CN)_6 + 2H_2O$, forms monoclinic prisms in combination with domes; it is more sparingly soluble in water than the ferrocyanides of the homologous bases, and can be employed as a means of obtaining pure pyridine. The ferrocyanides of the picolines are very readily soluble, that of *αα'*- and of *αγ*-lutidine are more sparingly soluble. The aqueous solutions of the ferrocyanides are tolerably stable in the cold, but decompose when heated above 70°. F. S. K.

Distillation of Salts of Pyridinecarboxylic Acids. By F. BLAU (*Ber.*, **21**, 1077—1078).—On dry distillation, the copper salt of picolinic acid yields an oil from which a strong base, probably *α*-*α*-dipyridyl, was isolated. This compound separates from water in crystals which melt at 70°; it is sparingly soluble in water, but dissolves readily in other solvents. F. S. K.

Amide of Dihydroxyisonicotinic Acid. By S. RUHEMANN (*Ber.*, **21**, 1247—1249).—Trichlorcitrazinamide (this vol., p. 255) combines with aniline to form a compound, $C_{18}H_{14}N_4O_3$, which is a strong base, and dissolves very readily in hydrochloric acid; it has also feebly basic properties and dissolves in ammonia. It is very sparingly soluble in alcohol, and is decomposed when boiled with glacial acetic acid.

A crystalline product, $C_6H_4N_2O_5$, is obtained by heating a hydrochloric acid solution of the preceding compound. This substance has acid properties and dissolves in ammonia, forming a yellow solution; it decomposes on heating, and its aqueous solution is turned deep brown by ferric chloride. Silver nitrate precipitates from an ammoniacal solution a yellow, gelatinous precipitate which blackens on heating. Heated with potash, ammonia is evolved, and a salt formed which is soluble in ether. F. S. K.

Quinolinesulphonic Acids. By A. CLAUS (*J. pr. Chem.* [2], **37**, 258—268; compare Abstr., 1887, 737, and this vol., pp. 296 and 501).—When quinoline is sulphonated with fuming sulphuric acid containing from 10 to 20 per cent. of anhydride at a temperature not exceeding 125—130°, three sulphonic acids are formed: the meta-, the ortho-, and an acid belonging to the ana-series. At a temperature of between 170—180° only the last two are obtained. These facts explain the contradictory statements of La Coste and Valeur, and Fisher, Bedall, and Riemerschmied. The three acids may be best separated by the fractional crystallisation either of the free acids or of their barium or calcium salts. The meta-acid (4 mols. H_2O) is the most soluble, and crystallises in small colourless needles. The potassium (1½—2 mols. H_2O) and sodium (3 mols. H_2O) salts are both somewhat hygroscopic. The calcium salt (4 mols. H_2O) crystallises from water in microscopic needles; the barium salt (4 mols. H_2O) is only indistinctly crystalline. The silver, lead, and copper salts are described. The sulphochloride forms a sticky mass, and the sulphonamide an indistinctly crystalline powder melting at 119° (uncorr.). On heating the silver salt with ethyl iodide in sealed tubes at 140°, the ethyl salt $C_9NH_6{\cdot}SO_3Et$ is formed. It melts at 275° (uncorr.).

When quinolinemetasulphonic acid is treated with bromine in the cold, additive products of little stability are formed; whilst at the temperature of the water-bath, the sulphonic group is displaced by bromine. A dibromoquinoline which sublimes in needles melting at 255°, and a tribromoquinoline melting at 199°, have been thus obtained.

Quinolinemetasulphonic acid when fused with potash yields a *hydroxyquinoline*, which softens at 165° and melts below 200°; whilst the ana-compound prepared synthetically from amidobenzenemetasulphonic acid yields an *hydroxyquinoline*, melting sharply at 224° (uncorr.).

Sodium quinolineorthosulphonate crystallises in needles with 5 mols. H_2O, the potassium salt with 2 mols. H_2O, and the copper salt in small green needles with 2 mols. H_2O. The lead salt is anhydrous.

Quinolineorthosulphonic acid cannot be directly brominated, but bromoquinolineorthosulphonic acid may be obtained by heating ethyl orthoquinolinesulphonate with bromine in sealed tubes at 180°. It decomposes at 350° without previously melting. The sodium salt (1 mol. H_2O) crystallises in needles; the lead, silver, and potassium salts are anhydrous. The copper salt (2 mols. H_2O) forms dark-green prisms. The sulphochloride melts at 88°, the sulphonamide at 185°, and the ethyl salt, $C_9H_5BrNSO_3Et$, at 98°.

On treating an aqueous solution of bromoquinolineorthosulphonic acid with bromine, a new *tribromoquinoline* crystallising in yellow prisms and melting at 205° is obtained. G. T. M.

Cinchoniline. By E. JUNGFLEISCH and E. LÉGER (*Compt. rend.*, **106**, 657—660).—*Cinchoniline*, $C_{19}H_{22}N_2O$, is obtained by treating the dihydriodide (this vol., pp. 380 and 507) with sodium hydroxide, which is then agitated with ether. The ethereal solution is washed with water and concentrated, when it deposits bulky, yellowish crystals, which are purified by recrystallisation. Cinchoniline crystallises more readily than its isomerides, and forms very large, colourless, anhydrous, right rhomboidal prisms. It melts without decomposition at 130·4°, and distils in a vacuum without undergoing rapid alteration; rotatory power of a 1 per cent. solution in alcohol of 97° at 75° $[\alpha]_D = +53·22°$; in $\frac{1}{2}$ a per cent. solution $[\alpha]_D = +50·3°$. In a 1 per cent. solution in dilute hydrochloric acid containing 2 mols. HCl for each molecule of base $[\alpha]_D = +59·15°$; if 4 mols. HCl $[\alpha]_D = +63·10°$. The base is only slightly soluble in water, but the solution is strongly alkaline to litmus and phenolphthaleïn. It dissolves readily in ethyl and methyl alcohols, chloroform, benzene, ether, and acetone. It reduces potassium permanganate in the cold, and when decomposed by heat yields the same products as cinchonine.

Cinchoniline forms basic salts which are feebly alkaline to litmus and normal salts which have no acid reaction; the majority of the salts are very soluble in water, and have a remarkable power of forming large crystals. The *basic hydrochloride*, $C_{19}H_{22}N_2O,HCl$, is extremely soluble even in cold water, but crystallises from the syrupy solution in very large, oblique, rhomboidal prisms which melt with decomposition at 226°. In an aqueous solution containing 1 per cent., $[\alpha]_D = +5·0°$

at 16°. The *platinochloride* forms small, orange-yellow prisms containing 1 mol. H_2O; the aurochloride, $(C_{19}H_{22}N_2O,2HCl,AuCl_3)_2 + H_2O$, crystallises in small, bright yellow, highly refractive prisms. The *basic hydrobromide*, $C_{19}H_{22}N_2O,HBr + 3H_2O$, is much less soluble than the basic hydrochloride, and forms long prisms which melt with decomposition at about 228°. The *basic hydriodide* is very soluble in water, and forms short, colourless prisms containing 1 mol. H_2O. It melts with decomposition at about 221°. The *normal hydriodide*, obtained by adding an alkaline iodide to a normal cinchoniline salt, forms short, hard, bright yellow anhydrous prisms, insoluble in water containing hydriodic acid. The *basic thiocyanate*,

$$C_{19}H_{22}N_2O,CNOH + H_2O,$$

forms long, silky, efflorescent needles only slightly soluble in cold water; the *basic chromate* forms an oily precipitate; the *basic oxalate* is extremely soluble, and crystallises in large prisms; the *normal oxalate* is likewise very soluble, and crystallises in needles; the *normal picrate* is amorphous.

Cinchoniline methiodide, $C_{19}H_{22}N_2O,MeI$, obtained by the action of methyl iodide on the base in presence of anhydrous ether, crystallises from alcohol in short, highly refractive prisms, and from water in long, colourless prisms. Both forms are anhydrous and melt with decomposition at about 233°. The *ethiodide*, obtained in a similar manner, crystallises from water or alcohol in highly refractive prisms containing 1 mol. H_2O. It is very soluble in water, alcohol, and chloroform, but is insoluble in benzene or ether. *Cinchoniline ethobromide* forms hard crystals, and is soluble in alcohol, but insoluble in ether.

C. H. B.

Ptomaïnes. By O. DE CONINCK (*Compt. rend.*, **106**, 858—861).—The flesh of cuttle fish, with the sepia bags removed, was allowed to putrefy, and the alkaloïds were extracted by Gautier's process. Several of the ptomaïnes described by Brieger were obtained, and two others of the composition $C_8H_{11}N$ and $C_{10}H_{15}N$ respectively.

The alkaloïd $C_8H_{11}N$ is a somewhat mobile, yellowish, strongly smelling liquid, very soluble in water, and also readily soluble in methyl or ethyl alcohol, ether, and acetone. When dry, it boils without decomposition at 202°; sp. gr. at 0° = 0·9865. When exposed to air, it becomes brown and absorbs moisture, and then boils at a lower temperature. The *hydrochloride*, $C_8H_{11}N,HCl$, forms deliquescent, white or yellowish radiating masses, very soluble in water at all temperatures. The *hydrobromide* is similar, but is less deliquescent and less soluble. The *platinochloride*, $(C_8H_{11}N)_2,H_2PtCl_6$, is deep yellow and almost insoluble in cold water, but soluble in hot water. It is somewhat stable, but decomposes more readily than the platinochlorides of the pyridine bases. Water at 80° or 100° decomposes it with formation of a pale brown powder $(C_8H_{11}N)_2,PtCl_4$, insoluble in cold water, and almost insoluble in hot water. The aurochloride is pale yellow, and is somewhat stable in the cold, but decomposes on heating.

The salts of this ptomaïne are less stable than those of the pyridine bases, and more closely resemble the salts of hydropyridines. If a cold solution of the hydrochloride is mixed with excess of gold chloride, some gold is reduced. C. H. B.

Ptomaïnes. By I. GUARESCHI (*Chem. Centr.*, 1888, 45, from *Ann. Chim. Farm.*, 87, 237—249).—The author has made some experiments with the object of excluding, if possible, the objection that has been urged with regard to these bases, namely, that they may not pre-exist, but arise from the action of the reagents (acid, alcohol, &c.) used in their extraction. From putrid fibrin, he has obtained a very satisfactory yield of a base, $C_{10}H_{13}N$, previously described by him, by making the mass alkaline with baryta in the cold, and extracting with ether and chloroform. This base pre-exists in the putrid fibrin. From the chloroform extract, another compound, $C_{11}H_{20}N_2O_4$, which appears to be an amido-acid, was obtained. It forms beautiful, shining plates melting at 248—250°, soluble in water and alcohol, but not readily soluble in chloroform. The watery solution is neutral or feebly acid, and gives all the general alkaloïd reactions. When a weak hydrochloric acid solution of the base is precipitated with platinum chloride, the platinochloride of the base $C_{10}H_{13}N$ is formed. J. P. L.

A Cadaveric Alkaloïd behaving like Strychnine. By C. AMTHOR (*Chem. Centr.*, 1888, 43, from *Chem. Zeit.*, 11, 288).—An alkaloïd with strychnine-like properties has twice been obtained from parts of a corpse eight days old.

The chief differences between this alkaloïd and strychnine are:—(1) It is less poisonous than strychnine when injected subcutaneously in the frog; (2) from alkaline solutions, ether dissolves but a very small quantity, whereas amyl alcohol dissolves it easily; (3) the taste is less bitter; (4) the precipitates with potassium ferrocyanide and ferricyanide, potassium chromate and picric acid are amorphous, those of strychnine crystalline; (5) the blue colour with potassium chromate and sulphuric acid is less persistent and less pure than the colour formed with strychnine. J. P. L.

Hæmoglobin of Dog's Blood. A. JAQUET (*Zeit. physiol. Chem.*, 12, 285—288).—Hæmoglobin was prepared from dog's blood, according to the method adopted by Zinoffsky (Abstr., 1886, 165) in the case of horse's blood, and then twice recrystallised. Elementary analysis gave the following percentage results, which for the sake of comparison are placed side by side with the numbers obtained by Zinoffsky:—

	Hæmoglobin of dog.	Hæmoglobin of horse (Zinoffsky).
C	53·91	51·15
H	6·62	6·76
N	15·98	17·94
S	0·542	0·390
Fe	0·333	0·335
O	22·62	23·43

W. D. H.

Action of Alloxantin on Blood. By N. KOWALEWSKI (*Chem. Centr.*, 1887, 1296, from *Med. Centr.*, **25**, 658—659, 676—678).—The author refers to a former paper (Abstr., 1887, 508) regarding the change into methæmoglobin that hydroxyhæmoglobin undergoes by the action of alloxantin, and shows in several instances how this change may take place under the influence of reducing agents. By the action of alloxantin on blood, the former reduces the oxyhæmoglobin to hæmoglobin, and is oxidised itself to such compounds as are able to change the reduced hæmoglobin into methæmoglobin. J. W. L.

Physiological Chemistry.

Chemistry of Fish; Analysis of American Specimens. By W. O. ATWATER (*Amer. Chem. J.*, **10**, 1—20; compare this vol., p. 308).—Tables are given of the composition of the flesh of fish, showing matters extracted by cold water and not coagulated; albumin coagulated from cold water extract; gelatin extracted by hot water; insoluble proteïn; fats, ash, and water; also tables showing the amounts of phosphoric, sulphuric, and hydrochloric acids in the ash. From these data, tables are constructed showing the relative value of various fish as foods. Analyses are also given of fresh and whole fish, and of salted and cured, or canned fish. H. B.

Occurrence of Fluorine in the Organism. By G. TAMMANN (*Zeit. physiol. Chem.*, **12**, 322—326).—The method adopted for the quantitative estimation of fluorine was as follows:—The substance under investigation was treated with powdered quartz and sulphuric acid. A current of dry air carried the silicon fluoride so formed through a narrow tube where it was decomposed with steam and the silicic acid collected on the walls of the tube, hydrofluosilicic acid being also formed; the latter was absorbed in aqueous potash, and evaporated to dryness; the residue was taken up with hydrochloric acid, the potassium silicofluoride precipitated with alcohol, filtered, and titrated with potassium hydroxide solution. Fluorine is well known to be a constant constituent of bone; it is also known to occur in ploughed earth and in wells. Horsford (*Annalen*, **149**, 202) found weighable quantities of fluorine in the human brain, and Salm-Horstman (*Ann. Phys. Chem.* **114**, 510) found that certain plants did not fully develop in the absence of fluorine.

In the present research, plants grown in culture liquids which did not contain fluorine, were found to die quickly when fluorine was added to such liquids; thus, the addition of 0·1 gram of potassium fluoride per litre caused death in these plants in 12 hours.

The different parts of the egg were investigated; the shell contained imponderable traces only; the white contained somewhat larger traces, but still imponderable; the yolk yielded weighable quantities; 84 grams of fresh yolk contained 0·0009 gram of fluorine. Attention is drawn to the fact that the brain and egg-yolk, tissues that contain much phosphorus, are also richest in fluorine. In other experiments, brain, cow's milk, and blood were found to contain small weighable quantities of fluorine.

From these experiments, certain conclusions are drawn, the chief purport of which is, that fluorine is of greater physiological importance in the animal economy than has hitherto been considered to be the case. W. D. H.

Digestion of Albumin. By J. Boas (*Chem. Centr.*, 1887, 1226, from *Zeit. Klin. Med.*, **12**, 231).—A comparative study of the three chief products, syntonin, hemialbumose, and peptone, of the artificial and natural digestion of albumin has been made. In artificial digestion, syntonin is formed at a very early stage with all the three kinds of albumin experimented on (fibrin, egg albumin, and scraped meat); the amount formed, however, varies considerably.

Hemialbumose is a constant product of fibrin digestion and a frequent product, though in much smaller quantity, of egg albumin digestion; it is altogether absent in the digestion of meat. Hemialbumose must be regarded more as a bye-product of digestion than as an intermediate step in the process, for, like syntonin, it is a product of the action of acid. Any hemialbumose formed is gradually converted into peptone, so that after long prolonged artificial digestion, syntonin and peptone, the first and last terms of the process, alone are present.

As far as the products are concerned, artificial and natural digestion are similar, but essential differences occur in the time of appearance and disappearance of the various modifications of proteïd. The artificial and natural digestion of fibrin are most alike. In artificial digestion, all three modifications are generally present from the beginning to the end of the digestion, but towards the end of natural digestion peptone is the almost exclusive product. J. P. L.

Food of Larval Bees. By A. v. Planta (*Zeit. physiol. Chem.*, **12**, 327—354).—The substance investigated was the juice or pap, the whitish sticky substance which the working bees store in the cells of the larvæ of the queens, drones, and workers. Leuckart (*Deutsche Bienenzeitung*, 1854, 1855) regarded it as the product of the true stomach of the working bees, which they vomit into the cells, in the same way that honey is vomited from the honey-stomach. Fischer and others regarded it as the product of the salivary glands of the bees. Schönfeld, in numerous papers, references to which are given, has more recently shown that Leuckart's original view is the correct one. He showed that the saliva can be easily obtained from the salivary glands of the head and thorax, and that it is very different from the food-juice deposited in the cells by the bees; and that, moreover, the juice is similar, both chemically and microscopically, to the contents of the bee's true stomach; he showed also from the consideration of certain anatomical and physiological peculiarities of the bee, such as the position of the mouth, the inability of the bee to spit, &c., that the view of this substance being saliva is quite untenable. Certain observers have to this replied that a bee cannot vomit the contents of its true stomach, because of a valve which intervenes between it and the honey-stomach; but Schönfeld has shown that the structure, mistaken by these observers for a valve, does not function as one, but is in reality an internal mouth, over which the animal has voluntary control, and by means of which it is able to eat and drink the contents of the honey stomach when necessity or inclination arises. By light pressure on the stomach, and stretching out the animal's neck, the contents of the stomach can be easily pressed out.

The present investigations entirely confirm Schönfeld's view that this substance comes from the bee's stomach. The subject was investigated from the point of view of its chemical composition, and also care was taken to investigate, individually, the juice as occurring in the cells of the three varieties of bees, queens, drones, and workers.

Some preliminary microscopical examinations of this substance yielded the following results, which are quite in accord with the subsequent chemical analyses:—

1. The food of the queen-bee larvæ is the same during the whole of the larval period; it is free from pollen grains, which have been reduced to a thickish but homogeneous juice by the digestive action of the bee's stomach.

2. The food of the larval drones is also, during the first four days of the larval period, free from pollen, and appears to have been completely digested previously. After four days their food is rich in pollen grains, which have, however, undergone a certain amount of digestion. The food stuff of the larvæ is probably formed from bee-bread.

The following table gives the average percentages obtained from several analyses in most cases:—

	Food stuff of		
	Queen-bees.	Drones.	Working-bees.
Water	69·38	72·75	71·63
Total solids	30·62	27·25	28·37
In the solids—			
Nitrogenous material	45·14	43·79	51·21
Fat	13·55	8·32	6·84
Glucose	20·39	24·03	27·65
Ash	4·06	2·02	—

All kinds are thus rich in nitrogen; all were of a greyish-white colour; that of the queen-bee was the stickiest, that of the workers the most fluid. Peptone appeared to be absent; the greater part of the nitrogenous material present was proteïd. The ethereal extract was in all cases acid, but formic acid was absent.

The sugar present was, in all cases, invert-sugar, whereas the sugar in pollen grains is invariably cane-sugar.

The table shows certain differences in the composition of the different kinds of larval food, more especially in the composition of the solids present. Its composition is, moreover, quite different from that of the bee's saliva, which, for instance, contains no sugar. The difference between the proportional amount of the different solids present in the different forms of larval food is a constant one, and no doubt this variation has in view the particular requirements of the larvæ in question. Certain small but constant differences were also observed in the chemical composition of the food of the larval drones during the first four days and at subsequent periods.

Not only is there a difference in the quality, but there is also one in the quantity of the food supplied. The juice from 100 queen-bee cells yielded 3·6028 grams of dry substance, that from 100 drones' cells 0·2612 gram, that from 100 workers' cells 0·0474 gram.

W. D. H.

Foddering of Horses, and the Circulation of Mineral Matter in the Horse. By E. Wolff and others (*Bied. Centr.*, 1888, 241—252).—The question as to whether the albuminoïds digested by the horse were really of higher value than a similar quantity of digested carbohydrates has not been satisfactorily answered; therefore a new set of experiments has been instituted with fodder rich and poor in nitrogen, and the work estimated by a dynamometer. Analytical tables are given showing the composition of the food and the manure produced, &c. The results obtained were: the digestible albumin has, above a certain minimum, no higher value as regards power of producing work than an equal quantity of starch-meal, or the starch equivalent of digestible cellulose and fat; field beans and maize are alike: to keep a horse of 500 kilos. weight in health and doing no work, 4200 grams weight daily of fodder is sufficient, provided that at least one-half consists of hay. As regards the circulation of the minerals in the horse, a large proportion of the lime (60—100 grams) is excreted as carbonate in the urine, causing that to be thick: of the magnesia one-third to two-fifths of the total quantity contained in the fodder appears in the urine, whereas the alkalis to the extent of 30 per cent. of the total is voided in the solids (sheep 5 per cent., oxen 10 to 12 per cent.). The phosphates also and the silicates are found altogether in the solids, whilst chlorine appears in the urine. As to the sulphates, they appear for the most part in the dung, and the more when the fodder is difficult of digestion and not too poor in nitrogen. The amount of urine voided is influenced by the percentage of digestible nitrogen and by the quantity of salts passing into the urine.

E. W. P.

Acetanilide and Acetotoluide in Relation to Animal Metabolism. By M. Jaffe and P. Hilbert (*Zeit. physiol. Chem.*, **12**, 295—321).—Schmiedeberg (*Arch. f. exp. Pathol. u. Pharmakol.*, **8**) has shown that aniline is probably oxidised in the body of the dog to form paramidophenol, which is passed in the urine in combination with sulphuric acid. A fresh examination into the fate of aniline compounds in the body seemed to be necessary, as it is known that the amido-group often appears to modify the fate of complex aromatic molecules in the organism. The acetyl-derivative of aniline (antifebrin) is moreover of practical interest from its use in therapeutics. Experiments were made on dogs and rabbits, the urine of these animals being examined after the administration of these substances; the crystalline substances separated from the urine were purified by recrystallisation, their reactions carefully studied, and finally they were subjected to elementary analysis. The following are the results obtained:—

1. The change in acetanilide is different in herbaceous and carnivorous animals. (*a.*) In the rabbit, it is oxidised to form paramidophenol, with complete elimination of the acetyl-group. (*b.*) In dogs there is a small formation of paramidophenol, but the chief change consists in a simultaneous oxidation of the aniline residue to orthamidophenol, of the acetyl-group to carboxyl, and next a union occurs with the formation of phenylcarbamic acid, the anhydride of which, orthohydroxycarbanil, is excreted in the urine. The latter can be isolated in large quantities by heating extracts of that secretion with hydrochloric acid.

Both in rabbits and dogs, the metabolic products of acetanilide are excreted in combination with sulphuric acid.

2. The three isomeric acetotoluides differ in their chemical behaviour in the animal body. (*a.*) Paracetotoluide is changed completely into paracetamidobenzoic acid, oxidation being limited to the methyl-group. (*b.*) Orthacetotoluide undergoes in dogs a decomposition completely analogous to that suffered by acetanilide. Whilst the methyl-group remains intact, a phenol is formed which combines with the product of oxidation of the acetyl-group; the end (excreted) product being methyl hydroxycarbanil or hydroxycarbamidocresol, which may be regarded as the anhydride of hydroxycresylcarbamic acid; this product in the urine occurs in combination with sulphuric acid, and rotates the plane of polarised light to the left. (*c.*) Metacetotoluide is in dogs and rabbits oxidised to form metacetamidobenzoic acid, which is passed as a lævorotatory compound which was not further investigated.

3. Of the three isomeric acetotoluides, the ortho-compound is the only one which has poisonous properties.

4. The para- and ortho-compounds do not affect the body temperature; the meta-compound causes a lowering of the temperature. This shows that no inference can be drawn from the chemical constitution of these compounds, as to their effect on body temperature, for orthacetotoluide is completely analogous to antifebrin; it, therefore, might be fairly expected to have antipyretic properties; but, as just stated, experiment shows that it has not. W. D. H.

Chylous Pericardial Fluid. By K. Hasebroek (*Zeit. physiol. Chem.*, **12**, 289—294).—A milky-looking fluid removed from the pericardium (*post-mortem*) of a patient at Strassburg (the clinical details of whose case are briefly given), was found microscopically to contain the histological elements of chyle, but it did not yield any fibrin—even when a drop of blood was added to it.

Chemical analysis gave the following result (in parts per 1000):—

Water	892·782
Solids	103·612
Proteïds	73·789
Cholesterin..................	3·340
Lecithin	1·771
Fat	10·767
Alcohol-extractives	2·048
Water-extractives	2·555
Salts	9·336

On comparing these numbers with those which are the results of analyses of pericardial fluid by other observers, the following table is obtained:—

	1. Present case.	2. (Gorup-Besanez).	3. (Wachsmuth).	4. (Hoppe-Seyler).
Water..........	892·782	955·1	962·5	961·78
Solids	103·612	44·9	37·5	38·22
Fibrin	—	0·8	—	—
Albumin	73·789	24·7	22·8	24·63
Extractives	20·481	12·7	—	—
Salts	9·336	6·7	—	—

The solids in the present case are thus far in excess of those in ordinary pericardial fluids; the large amount of fat is equalled only in the chyle among the fluids of the body.

By further contrast of the numbers obtained in the present case with those in the very few existing analyses of the chyle, or of chylous effusions into the pleura and peritoneum, it is found that there is a close agreement not only in the percentage of fat, but also of total solid proteïds, ethereal extract (cholesterin, lecithin, and fat). The conclusion is therefore drawn that the present case is not one of pericarditis, but of effusion from the lacteal vessels into the pericardium (chylopericardium). W. D. H.

Toxic Action of Alcohols and Artificial Bouquets. By Laborde and Magnan (*Chem. Centr.*, 1888, 18, from *J. Pharm.* [5], **16**, 448—454).—The following are the chief results of experiments on dogs:—Ethyl alcohol from all sources was found to have the same physiological action. Furfuraldehyde, which occurs with pyridine and other impurities in commercial alcohols, has strong toxic properties. The distillate of Jamaica rum boiling at 83°, when injected subcutaneously, causes strong convulsions.

Salicaldehyde, which is added to "Vermuth," "Bitter," and "Essence de renie de Prés," produces strong epileptic convulsions. Methyl salicylate, which is used as a substitute for oil of winter-green in "Vermuth" and "Bitter," also produces convulsions, although not of an epileptic form.

Finally, benzonitrile and benzaldehyde, which are added in small quantities to "noyau," produce tetanus and even death.

J. P. L.

Physiological Action of Nickel Salts. By LABORDE and A. RICHE (*J. Pharm.* [5], **17**, 1—11, 59—62, 97—105).—The action of nickel salts on the animal economy has been investigated with very contradictory results. Experiments were made on rabbits, &c., dogs and frogs by additions made to the food and by various methods of injection. Nickel sulphate, injected to the amount of 0·5 to 1·0 gram per kilo. body-weight, poisons a rabbit or dog. From 0·5 to 3·0 gram passed into the stomach produced vomiting and diarrhœa, but it is hardly possible to produce death this way. Nickel is considerably less active than copper, and its usual application in everyday life may be considered uninjurious. J. T.

Chemistry of Vegetable Physiology and Agriculture.

Saccharomyces Ellipsoideus and its Use in the Preparation of Wine from Barley. By G. JACQUEMIN (*Compt. rend*, **106**, 643—644).—Experiments have been made to determine whether *saccharomyces ellipsoideus* is a stable form or is merely an abnormal form of beer yeast developed under special conditions and liable to revert to the original form; but these experiments are not yet complete.

The action of elliptical yeast on barley wort produced a liquid with an alcoholic strength of 6° containing 60 grams of dry extract and 3 grams of ash per litre. It had the following percentage composition:—Alcohol, 4·80; reducing sugar, 1·00; dextrin, 3·00; albuminoïds, &c., 1·28; glycerol, 0·20; succinic acid, 0·04; acetic acid, 0·02; potassium hydrogen tartrate, 0·25; ash, 0·23; water, 89·18. The liquid has an agreeable flavour, and contains a greater proportion of albuminoïds and phosphates than wine from grapes. It differs from the latter in giving an abundant precipitate with tannin. The barley may be partially replaced by crushed wheat. Barley and wheat worts are cheaper than malt worts, and give products of equal quality. To obtain a liquid with an alcoholic strength of 8° or 10°, it is necessary to mix the wort with sugar or to use a greater proportion of grain.

In these experiments it was found that the elliptical wine yeast remained stable for 18 months, and it would therefore seem to be quite distinct from beer yeast.

When the wine obtained in this way from barley is distilled, it yields brandy of good flavour, whilst the brandy from wine produced by beer yeast has a bad flavour. C. H. B

Direct Assimilation of Vegetable Remains by Chlorophyll-containing Plants. By L. KOCH (*Chem. Centr.*, 1888, 13—14, from *Ber. deut. bot. Ges.*, **5**, 350—364).—The present observations relate to the saprophytic mode of life of *Melampyrum pratense*. The author describes the development of the root organs upon which the plant depends for its close attachment to the nutritive material. Compared with the mother root, they form moderately large balls, the thin-walled polygonal cells of which are filled with colourless, protoplasmic bodies of a curved rod-like form which appear to correspond with the bacteroïdes of the root-swellings of the Leguminosæ. Formed starch is not present. These cells play the part of reserve stores, and they break down when their contents are used up. All the author's observations lead to the conclusion that *Melampyrum* assimilates dead and not living parts of plants, consequently it is a saprophyte and not a parasite.

As the plant contains large quantities of chlorophyll it can readily supply its wants so far as non-nitrogenous food is concerned, and the nitrogenous food is probably supplied by the material stored in the polygonal cells—a conclusion which receives some support from the absence of formed starch in these cells. J. P. L.

Behaviour of Formose in contact with Vegetable Cells Deprived of Starch. By C. WEHMER (*Ann. Agronom.*, **14**, 40—41, from *Bot. Zeit.*, **45**, 713).—This research bears on the suggestion that the first product of the assimilation of carbonic anhydride in the plant cell is the formose of O. Loew, a substance formed by the condensation of formic aldehyde, and having a sweet taste, the power of reducing Fehling's solution, and some colour reactions in common with the sugars. It is, however, not fermentable; is without action on polarised light; does not yield the same acid by treatment with weak acids, nor the same substance by combination with phenylhydrazine as the true carbohydrates of the dextrose class. From this it seems doubtful whether it is a true carbohydrate, and the author's experiments strengthen this doubt, for they show that whereas leaves deprived of starch by being placed for some time in darkness have the power of forming starch when placed in solutions of dextrose and cane-sugar, they did not form any starch when placed for even 14 days in a 5 per cent. solution of formose. In this respect formose resembles erythrol. J. M. H. M.

Behaviour of Formose in Contact with Vegetable Cells Deprived of Starch. By C. WEHMER (*Bied. Centr.*, 1888, 268).—The leaves of *Fraxinus ornus*, *Rubia tinctorum*, *Syringa vulgaris*, and *Cacalia suaveolens*, formed no starch when in contact with a 5 to 10 per cent. solution of formose (from formaldehyde), whilst starch was formed from dextrose and saccharose, confirming the results previously given (preceding Abstract). E. W. P.

Absorption of Salts by Plants. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, **106**, 801—805 and 902—906).—*Amarantus caudatus*, *A. pyramidalis*, and *Portulacca oleracea* were grown in large pots containing about 50 kilos. of earth to which a large proportion of a soluble potassium salt had been added, care being taken that the quantity of water present was sufficient to keep the whole of the salt in solution.

Potassium sulphate was added in the proportion of 395·4 grams to 45·5 kilos. of soil. The observations afford further evidence of the tendency of potassium to accumulate in the leaves, but the quantity of potassium salts present is always below that required to form a saturated solution. If this limit is reached, the plant dies. The proportion of potassium in the flowers is about one-half, the proportion of potassium sulphate about one-tenth, of that in the leaves. On August 2nd, one-sixth of the total potassium was in the root, one-fifth in the stalks, and one-third in the flowers; on September 20th, one-fourth was in the root, one-fifth in the stalk, a tenth in the flowers, and half in the leaves. With the exception of the flowers, the juices of the plant become richer in sulphates as they travel from the roots to the leaves.

The general results show that endosmotic or other changes between the soil and the juices of the plants employed obey the usual law, the solution which is in contact with the roots remaining richer than the solution which passes through the roots into the plant. This is the more important, since in *Amarantus* the proportion of nitrates is much higher than in the soil, and hence these salts would tend to pass from the plant to the soil, and not *vice versâ*. The low proportion of sulphates in the stalks of *Amarantus* contrasts strongly with the tendency of the nitrates to accumulate in this part of the plant.

Potassium acetate was examined in a similar manner—327·7 grams of the salt being added to 45·5 kilos. of soil. The earth became alkaline owing to the decomposition of part of the acetate, and brown humous substances were formed which at first interfered with the growth of the plants. The following results were obtained on September 21st:—

	Root.	Stalk.	Leaves.	Flowers.
Moist plant	8·9	118·3	38·1	20·8
K_2O, absolute	0·119	1·529	0·636	0·231
K_2O, relative..........	5·2	5·9	8·0	5·5

The total quantity of potassium is not greater than in the same plants grown in ordinary soils; its accumulation in the stalks is in agreement with the authors' previous observations (*Ann. Chim. Phys.* [6], **5**, 547). The proportions in different parts of the plants are within the limits of variation in *Amarantus* under ordinary conditions, and hence it follows that the presence of a large quantity of potassium in the soil in a readily assimilable form has no marked influence on the absorption of this element by the plant.

Potassium nitrate was added in the proportion of 361·5 grams per 45·5 kilos. of soil. As in the other experiments, the total quantity of potassium in the plant and its general distribution were not affected by the presence of the large quantity of a potassium salt in the soil. On September 21st, a plant with a few flowers gave the following results:—

	Root.	Stalk.	Leaves.	Flowers.
Moist plant	55·4	383·8	124·5	13·3
K_2O, total............	0·897	6·444	2·490	0·187
K_2O, relative	5·1	7·7	6·8	4·6

These and other observations show that when the plant flowers the relative proportion of nitrates diminishes. A comparison of these results with those obtained with *Amarantus* growing in fields (*Ann. Chim. Phys.* [6], 8, 56) shows that the formation of potassium nitrate depends chiefly on the period of growth of the plant and not on the proportion of this salt existing in the soil. It attains the same order of magnitude in natural soils in which the ratio of nitrate to water is small as it does in artificial soils in which this ratio is very high, and hence is not dependent on the degree of saturation of the water in the soil. In the experiments described, the concentration of the nitrate solution in the soil was much greater than the possible concentration of the solution in the plant, whilst in the former experiments the solution in the plant itself was much stronger than the solution in the soil. It obviously cannot be assumed that the nitrates are absorbed from the soil, but they must be formed in the plant itself. C. H. B.

Production of Oxygen by Green Cells. By N. PRINGSHEIM (*Ann. Agronom.*, **14**, 41—43, from *Ber. deut. bot. Ges.*, **5**, 294—307).—The author, from his microscopical researches on the assimilation of carbonic anhydride by plants, concludes that the disengagement of oxygen, and decomposition of carbonic anhydride, hitherto considered as two manifestations of one and the same vital act, are really two separate phenomena, not simultaneous, and taking place in different spots, the latter occurring first in the interior, and the former afterwards on the surface, of the living cell. He supposes a third substance formed, or set at liberty, as the result of the decomposition of the carbonic anhydride, and having the power of giving up oxygen when it arrives at the surface of the cell. J. M. H. M.

Oxidation in the Plant. By J. REINKE (*Ann. Agronom.*, **14**, 43—45, from *Ber. deut. bot. Ges.*, **5**, 216—220).—The author considers that respiration is a purely chemical and not a vital phenomenon, and cites in support the fact that respiration is not arrested by the death of the cell, but that leaves killed by a prolonged exposure to ether vapour continue to emit carbonic anhydride a long time after death. Another explanation of this fact is given in the following Abstract.

J. M. H. M.

Continuation of Respiration in Dead Vegetable Cells. By W. JOHANNSEN (*Ann. Agronom.*, **14**, 134, from *Bot. Zeit.*, 1887, 162).—The evolution of carbonic anhydride due to respiration diminishes gradually in a dying plant, and ceases at the point of death. Oxidation recommences in the dead cells after a little time, but only as the ordinary oxidation of dead matter, due either to bacteria or to purely chemical agencies. The two phenomena may be distinguished thus: if a living cell is deprived of free oxygen, carbonic anhydride continues to be evolved by intramolecular respiration. If a dead cell be placed in the same conditions this does not take place. J. M. H. M.

Assimilation and Expiration of Plants. By U. KREUSLER (*Bied. Centr.*, 1888, 265—267).—This set of experiments was instituted to ascertain the influence of lower temperatures on the assimilation of plants. The plants observed were bramble, bean, castor-oil, and cherry laurel, the conditions of experiment and the methods employed were the same as on former occasions (this vol., p. 186), but the temperatures were lower. At 0°, the exhalation of carbonic anhydride was 17 to 20 per cent. of that which occurs at 20° in the case of the laurel and castor-oil plant; in the case of the bramble, the exhalation was only one-half of that at 10°. Assimilation at 0° is for the laurel only 8 per cent. of the possible maximum. E. W. P.

Absorption of Nitrogen by Plants. By HELRIEGEL and WILLFARTH (*Bied. Centr.*, 1888, 228—230).—Experiments were made in boxes in which were sown oats, peas, buckwheat, &c. It was found that those of the order *Papilionaceæ* were able to grow and flourish long after all the nitrogen present in the soil had been absorbed by them, whereas oats, &c., only grew as long as there was any of the nitrogen left that had been originally contained in the seed, &c. E. W. P.

Influence of Camphor on the Germination of Seeds. By A. BURGERSTEIN (*Landw. Versuchs-Stat.*, 1888, 1—18).—Commencing with a *résumé* of the work done by Vogel, Wilhelm, and Nobbe, and having pointed out the disagreement which exists between the results obtained, the author passes on to an account of his own experiments in which seeds of different ages and varieties of plants were grown and watered with a solution of camphor, time was also introduced as a factor in these experiments, the results being that camphor-water has an influence on germination, the influence depending on the time. A preliminary soaking in camphor-water has a detrimental effect on all seeds of whatever kind or quality they be, and this influence consists in a retardation of the process of germination, in a reduction in the percentage of germination, and in a reduction in the length of the sprouts during the earlier periods; moreover, absorption of camphor-water for only 12 hours weakens the germinative power. When the period of soaking was only 1 to 12 hours, then out of 27 seeds, 8 were accelerated in their growth, and 9 retarded in germination, whilst the remaining 10 were apparently alike as regards camphor compared with distilled water. No apparent change from normal colour was noticeable—the author cannot agree that camphor revivifies the germinative power of seeds, as Vogel states. E. W. P.

Distribution of the Ash in Trees. By WEBER (*Ann. Agronom.*, **14**, 143—144, from *Bot. Centr.*, **32**, 314).—A beech-tree, 150 years old, having been felled, a slice was cut off at every 5 metres of height, and from each slice were separated the layers corresponding to 30 annual ligneous rings. Analyses of the samples thus taken, showed that in a zone of the same age the quantity of ash increases regularly from the base of the trunk to the summit. At the lower part of the trunk the ash increases from the periphery to the centre up to a certain limit, beyond which it decreases towards the axis. In the slices cut off higher up the trunk, the increase of ash from periphery to centre goes on right through the section. The bark is much richer in ash than the wood.

As regards the composition of the ash, the potash increases from the exterior to the interior (from 23 to 43 per cent.) whilst the phosphoric acid, sulphuric acid, and magnesia diminish in the same direction, the magnesia falling from 29 to 11 per cent. and the phosphoric acid from 8 to 2 per cent. The variation in the lime is slight and irregular. In the bark, lime predominates greatly, amounting to 82 per cent., whilst the potash, magnesia, and phosphoric acid amount only to 4 to 1 per cent. J. M. H. M.

Phosphorus and Phosphoric Acid in Plants. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, **106**, 711—716).—Experiments with *Amarantus caudatus* and *A. pyramidalis*, protected from rain but freely exposed to the air, show that the plant absorbs both phosphorus and potassium from the soil in the early stages of its growth, though the amount of both, and especially of phosphorus, increases less rapidly than the weight of the plant. When inflorescence begins, the absorption of phosphorus practically ceases, but the absorption of potassium continues so long as the plant grows, and the increase in the quantity of this element during flowering is very considerable. The increase in the quantity of nitrogen is almost proportional to the increase in the weight of the plant up to the beginning of inflorescence, although somewhat smaller in the early stages of growth. When the plant flowers, the total quantity of nitrogen increases but little, and therefore the proportion of this element decreases.

In a soil containing about 8 grams of potassium acetate per kilo., the plants grew with some difficulty, but those which survived became much larger. They contained nearly twice as much potassium as under normal conditions, but the increase in the amount of phosphorus followed the ordinary law. The following example is typical of all the experiments.

	Weight of plant.	Phosphorus.	
		Absolute.	Relative.
May 31st................	1·693 grams.	0·0032	1·7
July 5th................	12·6 ,,	0·0265	0·73
August 2nd	14·68 ,,	0·0281	0·67
September 30th	22·58 ,,	0·0262	0·33

	Potassium oxide.		Nitrogen.	
	Absolute.	Relative.	Absolute.	Relative.
May 31st	0·0057	3·2	0·0041	2·3
July 5th	0·071	2·0	—	—
August 2nd	0·166	4·0	0·091	2·2
September 30th	0·251	3·0	0·103	1·2

On August 2nd, the plant had begun to flower, and on September 30th it had begun to die.

From these results it follows that manures containing phosphorus and nitrogen are of no value after the plant has begun to flower, but manures containing potassium may be useful throughout the whole period of growth. C. H. B.

Acidity of Cell Sap. By LANGE (*Ann. Agronom.*, **14**, 134—135, from *Bot. Centr.*, **32**, 236).—The author finds that acidification of the cell-sap during the night, and the disappearance of acid during the day, are changes not special to one or two groups of plants, but common to plants of all classes. The diurnal de-acidification is more energetic in the red half of the spectrum than in the blue. In this the author's results agree with those of Kraus and Warburg, and are opposed to those of de Vries. J. M. H. M.

Saccharine Matter in Peach-gum. By R. W. BAUER (*Landw. Versuchs-Stat.*, 1888, 33—34).—Peach-gum was boiled with 5 per cent. sulphuric acid for four hours, then neutralised with chalk, the filtrate after evaporation to a syrup extracted with alcohol, and the filtrate evaporated over sulphuric acid. The syrup remained unaltered some months, but after the introduction of a small quantity of pure dextrose, galactose, and arabinose, a mass of crystals was formed. After purification, these crystals seemed to be identical with galactose from agar-agar. E. W. P.

Injury to Plants by Kiln Smoke. By E. W. PREVOST (*Landw. Versuchs-Stat.*, 1888, 25—28).—The results obtained corroborate the observations of Schroeder (*Bied. Centr.*, 1884, 535) and Reuss, as regards the damage effected by smoke from furnaces; in this special case, the fumes came from brick-works, and the leaves of the various plants (rhubarb, pear, pine, larch trees, &c.), all showed brown spots on them, and in the case of the pines and larches the ends of the needles were affected; analyses show an increase of sulphuric acid in the leaf. The author is of opinion that leaves may be in an unhealthy state without any visible signs, these signs only appearing at a later date; he draws this conclusion from the fact that some samples which were collected and appeared to be healthy, showed minute spots on them after having been removed from the deleterious atmosphere for 12 hours. E. W. P.

Percentage of Sulphuric Acid in Plants Damaged by Sulphurous Anhydride. By E. MACH (*Landw. Versuchs-Stat.*, 1888, 52—53).—Hay made from grass which had been damaged by fumes from a cellulose factory in the Tyrol was submitted to analysis; the results showed that the percentage of water was much reduced, from 13·65 to 7·55 per cent., the pure ash was reduced from 9·77 to 8·36, whilst the sulphuric acid was raised in the dry matter from 0·54 to 0·818 and 0·96, and in the pure ash from 6·35 to 8·64 and 11·59. E. W. P.

Titanic Oxide in Soils. By G. F. MCCALEB (*Amer. Chem. J.*, **10**, 36—37).—Using Weller's hydrogen peroxide colorimetric test (Abstr., 1883, 381), a number of samples of soil from Virginia, U.S., have been examined, and all found to contain titanic oxide in quantities varying from 0·3 to 2·8, and even 5·4 per cent. H. B.

Sources of the Nitrogen of Vegetation. By J. B. LAWES and J. H. GILBERT (*Proc. Roy. Soc.*, **43**, 108—116).—Land which had been exhausted of nitrogen by successive crops of beans, gave a very large crop when sown with barley and clover. Numerous experiments were made to determine the source of the nitrogen. As the surface soil was richer in nitrogen after the crop had been grown, the nitrogen could not have been derived from that source. The clay subsoil was found to be susceptible to nitrification, especially in the presence of Leguminosæ, but the necessary secretion was a difficulty. In order to see if the acidity of the sap could account for the nitrogen obtained, soils were treated with organic acids. The amount of nitrogen obtained in this way was small, and less after long than after short contact. The nitrogen so taken up seems to exist in the soil in the form of amides, and the question arises whether the plant takes up the amide as such or converts it into ammonia and nitric acid. To test this, urea, uric acid, hippuric acid, quinine, ammonium phosphate, glycocine, creatine, and tyrosine were used in the water-culture method and in soil. Nitrogen was undoubtedly taken up, but in the soil experiments the organic compound appeared to have been decomposed; urea appears to be taken up as such. The evidence as to whether nitrogen is taken up from the air is very conflicting. The absorption, if any, has been attributed to electrical action, or to the agency of micro-organisms. In any case, the amount taken up would not suffice for the compensation usually supposed to take place. H. K. T.

Conversion of Nitrates in Soils into Nitrogenous Organic Compounds. By BERTHELOT (*Compt. rend.*, **106**, 638—641).—43·3 kilos. of moist earth, containing 72·3 grams or 1·669 grams per kilo. of organic nitrogen, was mixed with 361·5 grams of potassium nitrate, and a quantity of water sufficient to produce a 4 per cent. solution of the nitrate. The earth was then exposed to the air for six months, care being taken to protect it from rain. At the end of this time, the amount of organic nitrogen had increased by 16·4 grams or 0·3777 gram per kilo., a quantity equal to about one-fourth of the original organic nitrogen, and about one-third of the nitrogen in the potassium nitrate.

A similar quantity of earth with the same quantity of alkaline nitrate was planted with 11 roots of *Amarantus pyramidalis*, weighing 1·899 grams. After growth, the total weight of the dried plants was 197·2 grams, and they contained 5·83 grams of nitrogen. The quantity of organic nitrogen in the soil was practically the same as at the end of the first experiment, and was equal to about one-third of the nitrogen in the nitrate. The quantity of nitrogen and of nitrates in the plant was much below that found in former experiments, notwithstanding the large proportion of nitrate in the soil. It follows that the formation of nitrates in *Amarantus* is a complex process.

The assimilation by plants of the nitrogen existing in soils as nitrates is preceded or accompanied by a conversion of the nitrogen of the nitrates into nitrogenous organic compounds in the soil, either by the action of microbes or by pure chemical processes.

In all soils the formation of nitrates by the action of ærobic microbes is opposed by the action of the anærobic microbes, which produce fermentative and putrefactive changes and thus tend to reduce the nitrogen to nitrogenous compounds, or even to cause its liberation in the free state. The antagonism between these two classes of organisms explains the fact that nitrification reaches a limit before the whole of the nitrogen present is converted into nitrates. C. H. B.

Absorption of Nitrogen by Soils and Plants. By A. GAUTIER and R. DROUIN (*Compt. rend.*, **106**, 754—757, 863—866, and 944—947).—An artificial soil (A) was prepared by mixing 60 parts of Fontainebleau sand, washed with strong acids and then with water, and containing 0·5 per cent. of gelatinous silica, with 30 parts of pure precipitated calcium carbonate, 10 parts of pure washed kaolin, and 3 parts of neutral potassium phosphate. A second soil (B) was prepared by mixing A with 5 per cent. of ferric oxide; a third (C) by mixing 1100·25 grams of A with 22·5 grams powdered wood charcoal, washed with acids, and 2·25 grams of ulmic acid from sugar and hydrochloric acid; and a fourth (D) by mixing 1062·7 grams of A with 37·5 grams of ferric oxide, 22·5 grams of charcoal, and 2·25 grams of ulmic acid.

Quantities of the soils, with or without vegetation, were exposed to the air in pots in such a manner that they were completely permeable by the air, but were protected from rain. The total nitrogen was determined by a modification of Dumas' process, and the ammonia and nitrates by Schloesing's method. The quantity of soil used in each experiment was about 1200 grams.

A first series of observations was made with the four soils in which no plants were growing, the exposure to air extending from August 14th to October 31st, 1887, the soil being watered from time to time. With A, the total nitrogen diminished from 0·1181 to 0·1137 in one case and 0·1054 in another, the losses being respectively 0·0044 and 0·0127; with B, it diminished from 0·1252 to 0·0987 in one case and 0·1106 in another, the losses being 0·0294 and 0·0175 respectively.

When the soil contained organic matter, however, the results were different. With C, the nitrogen increased from 0·2344 to 0·3349, or a gain of 0·1005; with D, it increased from 0·2437 to 0·2592 in one case and 0·4451 in the other, the gain being 0·0155 and 0·2014 respectively. The small increase in the first case is due to the fact that the earth had settled in the pot, and was much less permeable to the air.

The same soils were sown with broad beans, which assimilate considerable quantities of nitrogen and are regarded by agriculturists as constituting a crop which enriches the soil in this element. The following results were obtained, the beans being sown on August 14th, and the plants cut down at the end of October:—

	Total nitrogen.		Increase.	Nitrogen in the soil.	
	Before.	After.		Before.	After.
Soil A....	0·3566	0·5372	0·1806	0·1151	0·1782
Soil B....	0·3666	0·5341	0·1675	0·1252	0 1558
Soil C....	0·4724	0·6797	0·2073	0·1126	0·3238
Soil D....	0·4806	0·7288	0·2482	0·1224	0·3145

These results show that soil free from organic matter loses part of its nitrogen when exposed to the air, but if it contains organic matter it is able to absorb nitrogen from the air independently of vegetation. When, however, the soil is supporting vegetation, a still greater quantity of nitrogen is absorbed by those which contained organic matter, and a considerable quantity is absorbed by soils which previously contained no organic matter, and hence of themselves absorbed no nitrogen. C. H. B.

Relation between Atmospheric Nitrogen and Vegetable Soils. By T. Schloesing (*Compt. rend.*, **106**, 805—809, and 898—902).—It has already been shown that nitrogen, like oxygen, cannot undergo any physical condensation in the pores of ordinary vegetable soil. If nitrogen is absorbed from the atmosphere, it must be fixed chemically or otherwise by the organic matter, since none of the inorganic constituents of the soil absorb nitrogen. Boussingault found that when air and soil were allowed to remain in contact for 11 years in hermetically sealed flasks, there was no increase in the quantity of nitrogen in the soil, but some of the nitrogenous organic matter was converted into nitrates at the expense of the oxygen of the air. In consequence of the direct contradiction between these results and those recently obtained by Berthelot and André, the author has repeated Boussingault's experiments with certain modifications.

The soil was enclosed in flasks with long necks, which were rendered vacuous, and pure air of known composition was allowed to enter. The necks were then bent over, and the open ends placed under mercury. The neck of each flask contained a quantity of calcium oxide, which absorbed the carbonic anhydride produced by the oxidation of the organic matter in the soil, and the absorption of oxygen was indicated by the rise of the mercury in the neck. Pure oxygen was introduced from time to time in order to maintain an excess of this gas in the atmosphere in the flask. After a sufficient length of time, the air remaining in the flask was analysed. By operating in this manner the accurate methods of eudiometry are substituted for the much less accurate plan of determining the amount of nitrogen in the soil. Complete details of the experiments are given in the second paper. Six soils of different character were employed. In each case, there was a large absorption of oxygen, with evolution of carbonic anhydride, the combustion of the organic matter in the soil proceeding to an extent varying with the nature of the soil. During this combustion, nitrates are formed, and the ammonia in the soil disappears. The variations in the volume of the nitrogen in the globes are not greater than the errors of experiment; the greatest variation actually observed corresponds with the absorption of 16 kilos. of nitrogen in 14 months by 4000 tonnes of soil, arranged in a layer 0·3 metre deep. C. H. B.

Mealy and Steely Barley. By W. Johannsen (*Landw. Versuchs-Stat.*, 1888, 19—23).—After several samples of barley had been moistened with an equal quantity of water, and then dried, it was found that the mealiness of the grain was dependent on the percentage of nitrogen, thus grains containing less than 1·41 per cent. N showed a degree of mealiness denoted by 95, whereas those containing 2·00 per cent. were classed as 30. Experiments further showed that if steely barley is slightly moistened and then dried, it will yield as good a malt as if it had been more mealy. E. W. P.

Sugars and Starch in Fodders and their Determination. By E. F. Ladd (*Amer. Chem. J.*, **10**, 49—53).—With wheat and its products, freshly prepared diastase gives an amount of starch (as determined by Fehling's solution) comparing favourably with that obtained by inversion with acid; but diastase hardly acts on the starch contents of hay and similar products. As regards the inversion by acids, it was found that with starch rather higher results were obtained by the use of sulphuric acid, but with hays and fodders more uniform and slightly higher figures were obtained by the use of hydrochloric acid. The amount of hydrochloric acid necessary is 3 to 5 c.c. for 5 grams fodder, or 3 grams starch and 150 c.c. of water; the action is complete in 11 hours. A number of analyses are given, showing the percentages of saccharose, glucose, starch, nitrogen-free extract and starch in various corns and fodders; the influence of the time of cutting and the action of various fertilisers are also briefly referred to. H. B.

Farmyard Manure. By P. P. Dehérain (*Ann. Agronom.*, **14**, 97—133).—As to the result of a survey of his own work and that of others, the author concludes that litter impregnated with the solid and liquid excreta of animals and placed upon a floor, undergoes the following changes:—

1. Solution of the vasculose and of a large proportion of the nitrogenous matter by the alkaline carbonates, the dissolved material constituting the dark brown colouring substance of the liquid drainings of the dung-heap.

2. Destruction of a great part of the cellulose of the litter by fermentation, with disengagement of methane and carbonic anhydride: the insoluble residue which persists after the loss of part of the nitrogenous matter, vasculose, and cellulose, consists of vasculose unattacked at the ordinary temperature; it is this residue, rich in vasculose partially altered by loss of water, which is often called "black butter."

3. Transformation of ammonia (arising from the fermentation of urea) into nitrogenous organic compounds, in great part soluble in alkaline liquids; this change is produced solely by living ferments.

4. During this fermentation, part of the nitrogen escapes in the free state, for when the manure is sufficiently moist very little loss of ammonia occurs. J. M. H. M.

Waste Products as Manure (Bone-meal). By A. PETERMANN (*Bied. Centr.*, 1888, 230—239).—These experiments, in which bone- and blood-meal mixed with potassium chloride, Chili saltpetre, or bone-ash were used, have been conducted for three years on clay and sandy soils in the neighbourhood of Gembloux. It was found that the simple addition of phosphates (bone-ash) to this sandy clay was of little or no value, but that when an addition of nitrogen was also made, as in bone-meal, then there appeared an increase in the yield of the crop; the results obtained from this mixture were far surpassed, however, by those obtained by the use of blood-meal, or phosphates with saltpetre and potash. The results obtained on the sandy soil were in all cases inferior to those on the heavy land: the best results were produced by the employment of blood-meal, bone-ash, and potash. Reviewing all his experiments made since 1880, the author comes to the conclusion that the various nitrogenous manures stand in the following order as regards manurial value: Saltpetre, dried blood, dissolved wool, bone-meal, raw wool, and leather-meal. E. W. P.

Addition of Wood-ashes to Superphosphates. By V. T. MAGERSTEIN (*Bied. Centr.*, 1888, 225—226).—An admixture of wood-ashes with superphosphates has long been known as advantageous, but the addition must not exceed 25 per cent., otherwise the lime which is thus added will cause a loss by reason of the formation of reduced phosphate. E. W. P.

Manuring Experiments with Various Phosphates. By E. GATELLIER (*Bied. Centr.*, 1888, 227—228).—As superphosphates are supposed to be reduced by the bases in the soil, and thus to become equal to insoluble phosphates, experiments were instituted to test the value of varieties of phosphates on clay soils in France; in all cases bone superphosphate (16 per cent. sol.) surpassed basic slag, ordinary superphosphate, &c. E. W. P.

Analytical Chemistry.

Thompson's Calorimeter. By SCHEURER-KESTNER (*Compt. rend.*, **106**, 941—944).—The proportion of oxidising mixture necessary for complete combustion varies with the nature of the coal and the proportion of ash which it contains. The author employed from 10·5 to 12·5 times the weight of the coal; with only 10 parts of oxidising mixture, the combustion is usually incomplete. The correction of 10 per cent. usually added to the results is much too low. Experiments with ignited wood charcoal showed that for the author's apparatus 15 per cent. was the true correction. This was used for samples of coal, the heat of combustion of which had previously been determined by Favre and Silbermann's method; the maximum difference was 1·25 per cent. The heat of combustion of 20 coals was determined by Thompson's calorimeter, and afterwards by Favre and Silbermann's apparatus. The variations were sometimes on the one side, sometimes on the other, the maximum difference being 3·5 per cent. In 11 cases, the difference was less than 2 per cent.

Although Thompson's calorimeter gives results of practical value, when an error of 2 or 3 per cent. is negligible, it is only worthy of limited confidence. Berthelot's calorimetric bomb would be much better. The main sources of error, as Stohmann has pointed out, are the heat of decomposition of the oxidising mixture and the heat of dissolution of the salts after combustion, since the proportion of each salt varies with each coal. Some finely powdered samples of coal which had been exposed to diffused light for 20 years in bottles not very tightly closed, were found to be completely unaltered. C. H. B.,

Improved Form of Gas Apparatus. By J. T. WILLARD (*Amer. Chem. J.*, **10**, 53—56).—The apparatus is essentially a combination of Elliott's (Abstr., 1887, 1137) and Frankland's. H. B.

Preservation of Solutions of Hydrogen Sulphide. By D. LINDO (*Chem. News*, **57**, 173—175).—The hydrogen sulphide is readily estimated in fresh solutions of this gas containing glycerol, camphor, boric acid, or thymol, by precipitation with silver nitrate and ammonia, filtering on a Gooch filter, drying, and weighing. In old solutions containing glycerol, silver nitrate does not answer, therefore the author employs sodium arsenite and hydrochloric acid for the precipitation. This precipitate is, however, troublesome to wash, and is best kept as small as possible, or if precipitated along with prepared asbestos, by adding some of the latter to the solution before precipitation, it may be washed with comparative ease.

From numerous experiments made in Jamaica in closed and open bottles at an average temperature of 26°, the author concludes that there is no advantage derived from the use of glycerol for the preservation of solutions of hydrogen sulphide.

Moreover, the other substances mentioned above do not prevent loss in strength by escape of gas, but camphor and thymol appear to retard oxidation. D. A. L.

Rapid Determination of Hydrogen Peroxide. By CONTAMINE (*Dingl. polyt. J.*, **267**, 238).—A few c.c. of the solution under examination is introduced into a glass tube divided into tenths of a c.c., and sealed at one end. Having previously neutralised the solution with ammonia, the volume is read off. A few crystals of potassium permanganate enclosed in tissue paper are then added, after which the aperture is closed with the finger and the tube shaken vigorously. It is then opened under water and the volume read off. The difference between the two readings gives the quantity of oxygen contained in the hydrogen peroxide solution. The method is sufficiently accurate to be used in works for determining the quantity of hydrogen peroxide in bleaching solutions. D. B.

Supposed Occurrence of Hydrogen Peroxide in Animal and Vegetable Juices. By T. BOKORNY (*Ber.*, **21**, 1100—1102).—Wurster's tetramethylparaphenylamine reaction (Abstr., 1887, 295) is useless as a test for hydrogen peroxide in animal and vegetable juices, since the paper is turned blue by very many compounds, such as nitrites, moist silver oxide, quinone, aldehyde, acetone, &c. For this reason, the reaction is no proof of the presence of hydrogen peroxide. Experiments have shown that living protoplasm does not give the ordinary reactions for hydrogen peroxide. F. S. K.

Gravimetric Estimation of Chlorine. By F. STOLBA (*Chem. Centr.*, 1887, 1240, from *Listy. Chem.*, **11**, 224—225).—In the case of small quantities of chlorine (up to 80 miligrams) in water, &c., the author precipitates the chlorine as silver chloride, collects the precipitate on a large Schleicher-Schuell filter-paper, dries, and so folds the paper that the precipitate is enveloped at the point in many folds of paper, the paper is very slowly carbonised in a platinum capsule, the carbon burnt off at a low temperature, and the remaining spongy silver weighed and tested as to its complete solubility in nitric acid. J. P. L.

Volumetric Determination of Sulphuric Acid. By A. GAWALOWSKI (*Zeit. anal. Chem.*, **27**, 152—159).—The principle of the method is identical with Wilsing's (Abstr., 1887, 181). The titration with sodium carbonate is, however, made in the cold after the addition of a few drops of alcohol. Boiling is said to favour the end reaction, but not to be absolutely necessary. The mixture of the sulphate with the barium chloride should be allowed to remain for ¼ or ½ hour before titrating the excess, and a similar interval should be allowed before finally judging of the completion of the titration with sodium carbonate. Seminormal solutions are recommended. The test analyses show errors of 1 per cent. in both directions. M. J. S.

Volumetric Estimation of Sulphuric and Phosphoric Acids. By J. T. WHITE (*Chem. News*, **57**, 165—166; 187).—Sulphuric acid in combination with fixed alkalis may be estimated by titration with silver nitrate and potassium chromate in the following manner:—Precipitate the solution with excess of barium chloride, and remove the barium remaining in solution with ammonium carbonate, then evaporate, ignite, and titrate the resulting alkaline chlorides in the ordinary fashion. If phosphoric acid is also present, precipitate it beforehand with magnesium chloride and ammonia. One portion of this filtrate is then evaporated with ammonium chloride, and the ignited residue titrated; whilst another portion is treated as above for sulphuric acid; the difference between the two results is the chlorine due to the decomposed sulphates. To estimate phosphoric acid in alkaline phosphates, decompose chlorides if present by evaporation with sulphuric acid, neutralise with soda, precipitate with excess of silver nitrate solution, neutralise with calcium carbonate, and titrate the excess of silver nitrate in the usual way. The presence of sulphuric acid does not interfere, as the solution is kept sufficiently dilute to dissolve silver sulphate. D. A. L.

Estimation of Total Nitrogen. By HOUZEAU (*Chem. Centr.*, 1888, 82—83, from *Pharm. Centr.*, **28**, 627—628).—The process depends on the fact that all nitrogenous substances yield the whole of their nitrogen in the form of ammonia when heated with sodium acetate, sodium thiosulphate, and soda-lime.

The mixture of sodium acetate and thiosulphate is prepared by melting equal parts by weight of both salts in their water of crystallisation on a water-bath and powdering the cooled residue.

The combustion is performed in precisely the same manner as in the Will-Varrentrap process, about 2 grams of the mixture with 2 grams of soda-lime at the end of the tube supply the necessary indifferent gases to drive off the last of the ammonia. J. P. L.

Sources of Loss in the Determination of Nitrogen by Soda-lime. By W. O. ATWATER and E. M. BALL (*Amer. Chem. J.*, **10**, 113—119).—The following directions are given as being necessary. The anterior portion of the tube must be tightly packed with coarse soda-lime, not with fine, and there must be no appreciable open channel along the upper portion of the tube, otherwise, losses amounting to 6·4 per cent. of the nitrogen may occur. The anterior layer is the first part of the tube heated. The time of combustion should not be too protracted, 2½ hours for instance, as this may introduce an error of 2·8 per cent., and if the tube is not packed as above, an error of even 77 per cent. may occur. Moreover, the results are far more concordant among themselves, and agree perfectly with those given by Kjeldahl's method when the above conditions are carried out. Substances like caseïn yield all their nitrogen as ammonia under these conditions, but strychnine yields only a small fraction, and the whole cannot be obtained even by Kjeldahl's method. H. B.

Absorption of Ammonia by Acid Solutions in Nitrogen Determinations. By I. S. HAYNES (*Amer. Chem. J.*, **10**, 111—113).—The absorption of the ammonia is quite complete if double the amount of acid theoretically necessary is employed, even when large quantities of inert gases are present, and when the gases are passed rapidly through the acid, say at the rate of 90 bubbles per minute, the combustion occupying only 12 minutes. Great attention must, however, be paid to the asbestos plug in the anterior portion of the tube being packed sufficiently tightly, or particles of soda-lime will be carried forward into the acid. H. B.

Examination of Wine for Nitric Acid. By E. BORGMANN (*Zeit. anal. Chem.*, **27**, 184—187).—The method proposed by Egger (Abstr., 1885, 842), for detecting the addition of water to wine by testing for nitrates with diphenylamine and sulphuric acid, is not in all respects trustworthy. Wines which on analysis give results incompatible with an addition of water are sometimes found to show the nitric acid reaction distinctly. Some of the waters of Rhenish Hesse, however, contain so much nitric acid (in one case 1 gram per litre), and the reaction will detect so small a trace (1 part in two millions of wine when Egger's concentration method is employed), that the mere rinsing of the casks with such water would introduce enough nitrate to give the reaction. On the other hand, wines to which nitrate has actually been added, have failed to give any indication of its presence after the lapse of a few months. M. J. S.

Determination of Phosphoric Acid. By F. BENTE (*Chem. Centr.*, 1887, 1241, from *Rep. anal. Chem.*, 7, 533—534).—The low and discordant results obtained in the analysis of basic slag which were assigned by the author (Abstr., 1887, 397) to the insufficient time allowed for complete precipitation, are probably brought about by the varying amount of chlorine in solution. For that reason he now employs sulphuric acid to dissolve the slag, as Brunnemann and Loges have recently done. J. P. L.

Volumetric Determination of Phosphoric Acid. By C. SCHINDLER (*Zeit. anal. Chem.*, **27**, 142—146).—The molybdenum in the yellow phosphomolybdate precipitate is determined by the author's volumetric method (p. 758), and the phosphoric acid is calculated therefrom. A precipitate of constant composition is secured by adding citric acid to the ordinary molybdate solution (15 grams to 1 litre). 50 c.c. of the nitric acid solution of the phosphate (0·5 gram of substance) is mixed with so much of a solution of ammonium nitrate (750 grams per litre), that after the addition of the molybdate the mixture shall contain 25 grams of ammonium nitrate per 100 c.c. Then for each 0·1 gram of phosphoric anhydride, 100 c.c. of molybdate is added, and the mixture is heated in a water-bath to about 58°. The precipitate is allowed to deposit for 10 minutes, the supernatant liquid is filtered, and the precipitate is washed three or four times with dilute ammonium nitrate (100 grams with 10 c.c. of nitric acid per litre). It is then dissolved in 3 per cent. ammonia, treated with 10 to 20 c.c. of Fresenius' magnesia mixture, and made up to 250 c.c. After shaking, it is filtered: 50 c.c. of the filtrate is acidified with acetic acid, diluted to 300 c.c. with hot water, and titrated with lead acetate. Comparative determinations on a variety of materials show a close agreement with the magnesia method. M. J. S.

Detection of Small Quantities of Arsenic in Fabrics, Yarn, and Wall Papers. By R. FRESENIUS and E. HINTZ (*Zeit. anal. Chem.*, **27**, 179—182).—25 grams of the material is placed in a ½ litre stoppered retort of Bohemian glass, and 250 c.c. of hydrochloric acid of 1·19 sp. gr. is added. The neck of the retort is bent so that the part near the bulb is inclined upward, whilst the other part slopes downward. It is connected with a condenser, which is also fitted air-tight to a tubulated receiver, and this again to a Peligot's tube. The receiver and tube contain water, and are kept cold. After digestion for an hour, 5 c.c. of a cold saturated solution of ferrous chloride is added, and the liquid is slowly raised to boiling, which is continued until frothing stops the distillation. A further quantity (100 c.c.) of hydrochloric acid is then added and distilled over. The united distillates are diluted to 800 c.c., and saturated with hydrogen sulphide, first warm and then cold. The arsenious sulphide, which contains organic matter, is filtered off on an asbestos filter formed in a stop-cock funnel. After partial washing, it is treated with a solution of bromine in hydrochloric acid (1·19), and the solution, washed through with the same acid, is again distilled with ferrous chloride in an apparatus similar to the former, but smaller. The distillate now gives arsenious sulphide free from organic matter, and requiring only to be purified from sulphur. Test analyses gave satisfactory results. The residue in the retort was found to be free from arsenic.

M. J. S.

Some Methods of Separating and Determining Arsenic, Antimony, and Tin. By E. LESSER (*Zeit. anal. Chem.*, **27**, 218—221).—The oxalic acid method of F. W. Clarke (*Chem. News*, **21**, 124) gives good results. To the solution, which should be neutralised as far as possible, 35 to 40 parts of oxalic acid are added for each part of tin present. The liquid is then heated whilst being saturated with hydrogen sulphide. The precipitate is dissolved in ammonium sulphide, and the solution acidified with oxalic acid is again saturated whilst hot with hydrogen sulphide. The two filtrates which contain the tin are concentrated, mixed with ammonia, ammonium sulphide, and acetic acid, and the precipitate converted into stannic oxide for weighing. The arsenious and antimonious sulphides are dissolved from the filter by ammonium sulphide, oxidised with hydrochloric acid and chlorate, and the arsenic precipitated as magnesium arsenate, after addition of tartaric acid. The precipitate requires resolution and reprecipitation to free it from basic magnesium tartrate.

Vohl boils the strongly acid solution of the three metals, and adds sodium thiosulphate until the precipitate becomes white. The precipitate contains the arsenic and antimony. Lesser finds the separation of tin and arsenic by this method satisfactory, but that of tin and antimony inaccurate.

De Clermond and Frommel's method of separating arsenic from the other two metals by boiling the sulphides with water until they are completely converted into oxides does not give good results, as the oxides of tin and antimony are not absolutely insoluble. Neither is the separation of arsenic from antimony by strong hydrochloric acid satisfactory.

Lesser weighed his antimony as tetroxide, but recommends weighing as sulphide, for which purpose the precipitate, freed from sulphur by carbon bisulphide, is washed into a weighed porcelain crucible by ammonium sulphide, and dried in the covered crucible in the air-bath at 200—230°, for at least nine hours. M. J. S.

Separation and Estimation of Boric Acid. By H. N. Morse and W. M. Burton (*Amer. Chem. J.*, **10**, 154—158).—The substance, if insoluble in water, is heated with pure potash in a nickel crucible for two hours, so as just to maintain the whole in a state of fusion. The mass is extracted with hot water, which if iron is present, must amount to 100 parts for every part of potash employed, and the whole is heated on a water-bath for a considerable time; this precaution is necessary, as otherwise the iron is not completely removed, and ferric sulphate being soluble in alcohol, its presence is not admissible. The filtered solution is evaporated to 10 or 12 c.c., and after addition of a few drops of tropæolin, OO, a not too dilute sulphuric is added, until exactly neutral. The solution now containing only neutral salts of the alkalis, boric, silicic, and carbonic acids, and not exceeding 20 c.c. in volume, is dried by slowly stirring into it pure copper sulphate (free from iron and from chlorides) that has been dehydrated at 150°. The powdered mass is transferred to a filter-tube, and extracted with absolute alcohol (dried over copper sulphate) in six lots of 15 c.c. each. The alcoholic filtrate is run into a quantity of standard baryta solution, the excess of baryta is converted into the carbonate by a current of carbonic acid, and the whole is then evaporated and ignited in a platinum dish over a good burner. The residue is a mixture of barium metaborate and carbonate; the amount of boric anhydride is found thus:—as the molecular weight of boric anhydride minus the molecular weight of carbonic anhydride is to the molecular weight of boric anhydride, so is the weight of residue minus the theoretical weight of the barium carbonate obtainable from the baryta used, to the weight of boric anhydride present. The analyses quoted are exceedingly concordant and satisfactory. H. B.

Estimation of Silver in Alloys of Silver and Copper. By H. Rössler (*Dingl. polyt. J.*, **267**, 570—572).—Gay-Lussac's wet assay is recommended in cases where great accuracy is required, providing that the alloy to be assayed is melted, and a sample taken from the fused mass. This is necessary, as alloys of silver and copper in solidifying do not remain homogeneous throughout, the inner and outer parts of the alloy containing different proportions of silver.

D. B.

Estimation and Separation of Metals by means of Sodium Pyrophosphate. By G. Vortmann (*Ber.*, **21**, 1103—1106).—The behaviour of metallic salts towards sodium pyrophosphate and acetic acid can be employed as a means of separating the metals, and the pyrophosphates thus obtained, being insoluble in water, dilute acetic acid, and solutions of ammonium salts, can be made use of for quantitative determinations.

Copper salts give with sodium pyrophosphate a bright blue precipitate, soluble in excess of the reagent; on adding acetic acid, a bright blue crystalline precipitate is obtained, the precipitation is, however, incomplete, and can be entirely prevented by the addition of sodium tartrate or sodium thiosulphate.

Cadmium salts give a precipitate soluble in excess. Acetic acid reprecipitates the salt almost completely even in the cold; by evaporating to dryness and digesting the residue with water, reprecipitation is complete. The addition of sodium tartrate or thiosulphate does not hinder the precipitation.

Manganese salts yield a precipitate, soluble in excess, but completely reprecipitated by acetic acid; sodium tartrate does not prevent the precipitation.

Zinc salts behave similarly, but reprecipitation is complete only when the solution is evaporated to dryness and the residue taken up with water; sodium tartrate retards reprecipitation.

Cobalt salts give a gelatinous precipitate, soluble in excess; on shaking or heating gently, the solution becomes gelatinous but not if sodium tartrate is added. Acetic acid reprecipitates the cobalt salt. Presence of sodium tartrate does not prevent reprecipitation.

Nickel salts behave similarly, but the addition of sodium tartrate prevents the reprecipitation with acetic acid.

Ferrous salts yield a precipitate soluble in excess, but completely reprecipitated on addition of acetic acid.

Ferric salts give a precipitate soluble in excess and not precipitated by acetic acid; on addition of acetic acid and sodium sulphite, reprecipitation is complete.

Aluminium salts give a precipitate soluble in excess, but completely reprecipitated by adding acetic acid and boiling; the addition of sodium tartrate prevents reprecipitation.

Uranic salts give a precipitate soluble in excess and not reprecipitated by acetic acid.

Chromic salts give a bright green precipitate which is scarcely soluble in excess even on boiling. Acetic acid prevents the precipitation of chromic salts, but the solution becomes turbid; the addition of sodium tartrate prevents the turbidity.

From the above results it will be seen that by means of sodium pyrophosphate copper can be separated from cadmium, cobalt from nickel, manganese and zinc from ferric salts, manganese from aluminium and uranium, and ferrous salts from aluminium and uranium, possibly also from chromium and ferric salts. Cadmium, zinc, manganese, cobalt, nickel, possibly also iron and aluminium, can be estimated as pyrophosphates. F. S. K.

Reduction with Lead. By F. Stolba (*Chem. Centr.*, 1887, 1240, from *Listy. Chem.*, **11**, 225—226).—Under certain conditions, lead reduces iron, chromium, and tin chlorides almost as quickly and completely as zinc. Lead, however, only reduces stannic chloride to stannous chloride. Small quantities of nitric acid do not influence the reduction. J. P. L.

Colorimetric Estimation of Minimal Quantities of Iron. By Sabanéeff and Kislakowski (*Chem. Centr.*, 1888, 84, from *Pharm. Zeit. Russ.*, **26**, 776—777).—For the estimation of minimal quantities of iron in mineral waters, &c., the colorimetric method with ammonium sulphide leaves nothing to be desired, either from the point of rapidity or precision. It is also free from the errors which organic substances may cause in titrating iron with potassium permanganate or alkaline chromate.
J. P. L.

Determination of Iron in Iron Ores by the Tartaric Acid Method. By L. Blum (*Zeit. anal. Chem.*, **27**, 146—151).—A source of error in the precipitation of iron by ammonium sulphide from solutions of ores containing magnesium and phosphoric acid, exists in the simultaneous precipitation of magnesium phosphate, the phosphoric acid of which subsequently comes down with the ferric oxide when the solution of the sulphide is precipitated by ammonia. With ores containing only a small amount of phosphoric acid and for technical determinations, the error can be practically got rid of by largely diluting the solution, heating it before adding ammonium sulphide, and before filtering allowing it to remain only just long enough for the ferrous sulphide to subside (about half an hour).

Fresenius points out in a footnote that a more certain way would be to precipitate the iron with most of the alumina as basic salts, before separating by ammonium sulphide in a tartrate solution, or else to allow the solution made alkaline by ammonia to remain for some time and to filter before the addition of ammonium sulphide.
M. J. S.

Estimation of Chromium in Iron or Steel in presence of Phosphorus. By J. O. Arnold and H. J. Hardy (*Chem. News*, **57**, 153—155).—As the method of analysis previously described (Abstr., 1880, 646) is not accurate in the presence of much phosphorus, the authors have modified it. They observed that under suitable conditions chromium is readily precipitated as a basic phosphate of constant composition, and they base the improved method on that fact. They take 2·4 grams of metal, and after the fusion make the precipitate and solution together up to 301 c.c., then 250 c.c. of the clear solution (containing the chromium from 2 grams of metal) is acidified with hydrochloric acid and boiled (no alcohol is added, the necessary reduction being effected by the nitrous gases evolved), excess of sodium phosphate is now added, then dilute ammonia in slight excess, and the whole heated until the solution is clear and colourless. The precipitate is dissolved in hydrochloric acid, carefully evaporated to dryness, redissolved by boiling with a few c.c. of hydrochloric acid and filtered. The chromium phosphate is now reprecipitated from the diluted solution by a slight excess of dilute ammonia, washed carefully, dried, and weighed as $Cr_6P_4O_{19}$. This method has given good results in the authors' hands. Titrating the chromium in the precipitated phosphate by means of permanganate gives low results.
D. A. L.

Volumetric Determination of Molybdenum and Lead. By C. Schindler (*Zeit. anal. Chem.*, **27**, 137—142).—Ammonium molybdate mixed with lead acetate gives a precipitate of lead molybdate, $PbMoO_4$, which is perfectly insoluble in acetic acid. An excess of the molybdate is detected by bringing a drop in contact with a solution of tannin (1—300). One part of the molybdate in 400,000 of water gives a visible yellow colour with tannin; strong solutions a blood-red. The lead acetate solution contains 40 to 50 grams (with some acetic acid) in the litre. The molybdate solution is made by dissolving 20 grams in 800 of water, adding ammonia until the turbidity disappears, and diluting until it corresponds with the lead solution in strength. To make a titration, the molybdate solution is acidified with acetic acid and diluted to 300 or 400 c.c. with hot water; a small excess of the lead solution is added, and then molybdate until a large drop of the clear, upper liquor brought in contact with a drop of the tannin solution on a porcelain plate gives a distinct orange colour. The exact strength of the lead solution should be determined by means of weighed quantities of pure ammonium molybdate, $[(NH_4)_6Mo_7O_{24} + 4H_2O]$, or, if otherwise ascertained, a deduction of 0·1 c.c. of molybdate solution must be made to allow for the excess required (207Pb to $144MoO_3$). The tannin solution must be freshly prepared.

M. J. S.

Determination of the Amount of Soda and Lime requisite for Purifying Water. By O. BINDER (*Zeit. anal. Chem.*, **27**, 176).—A measured quantity of the water is mixed with an excess of saturated lime-water of known strength. The mixture is warmed to between 50° and 80°, cooled, made up with boiled distilled water, filtered, and the excess of lime in the filtrate titrated with sulphuric acid, using phenolphthaleïn as indicator. The amount of lime required by the water is greater than that which corresponds to the temporary hardness, since magnesia as well as magnesium carbonate is precipitated both from the hydrogen carbonate and from the sulphate and chloride, and because a certain quantity of lime is consumed by free carbonic acid and by organic matters.

For the quantity of soda required, 250 c.c.of the water is evaporated to dryness with 5 c.c. of normal sodium carbonate solution. The residue is dissolved in water, filtered, and the excess of soda titrated by an acid and methyl-orange. It is advisable in practice to use 10 grams per cubic metre above the quantity thus indicated.

M. J. S.

Ash Determination. By L. REESE (*Zeit. anal. Chem.*, **27**, 133—136).—The incineration is carried on in a tube through which a rapid current of air is being drawn. Substances which are liable to intumesce and leave a difficulty combustible coal can thus be burnt in one-third to one-half of the time and at a lower temperature than would be required in a crucible. The substance is placed in a porcelain boat which is inserted into a short piece of combustion tube, narrowed at one end, and containing at that end a plug of platinum gauze to arrest any particles of ash carried off by the air current. The tube has a spiral of platinum wire round it to prevent adhesion to the outer tube in which it is placed to be heated.

M. J. S.

Quantitative Determination of Paraffin. By R. Zaloziecki (*Dingl. polyt. J.*, **267**, 274—279).—The principle of the author's method is the same as that on which Engler and Boehm's process is based, a precipitating agent being employed which has no solvent action on paraffin, but dissolves the accompanying impurities. It was found by experiment that paraffin is insoluble in ethyl alcohol of 75° Tralles, its solubility in amyl alcohol is diminished by the addition of ethyl alcohol, whilst the solubility does not decrease proportionately with reduction of temperature. The method, which is a simplification of the Engler and Boehm process, is as follows:—10 to 20 c.c. or grams of the paraffin under examination is mixed with five times the amount of amyl alcohol and the same volume of ethyl alcohol of 75° Tr., and the mixture kept for one hour at a temperature not exceeding 4° if possible. It is filtered through a dry filter and the residue washed with a cold mixture of 2 parts of amyl alcohol and 1 part of ethyl alcohol (70° Tr.). The paraffin is then extracted from the residue by means of ether in an apparatus illustrated in the original paper. The filter and contents are placed in a glass tube open at both ends, which is put into a wider tube. The latter is fitted into a tared flask. After extraction the flask is dried at 125° and weighed.

The method is adapted to the determination of paraffin in crude oils, in which case it is recommended to use twice the amount of mixed alcohols. By the same method, paraffin in fatty acids, neutral fats, resins, and resin oils may be determined with comparative accuracy. It is, however, inapplicable to the estimation of paraffin in waxes (beeswax, for instance), owing to their insolubility in alcohol.

D. B.

Determination of Acetone in Methyl Alcohol, Wood Spirit, and Acetone. By E. Hintz (*Zeit. anal. Chem.*, **27**, 182—184).—Krämer's method (Abstr., 1880, 826) gives good results only when the liquid under examination does not contain more than 1·5 per cent. of acetone. Liquids with a higher percentage must be diluted with water. Blank experiments are necessary to obtain a correction for the solubility of the iodides in ether, and in the case of wood spirit a blank in which the iodine is omitted must be made in order to correct for tarry matters which precipitate. M. J. S.

Plastering of Wine. By P. Carles (*J. Pharm.* [5], **17**, 11—14). —The volumetric and gravimetric estimations of potassium sulphate in wines often disagree. This is largely due to the modern practice of adding sulphurous anhydride in solution instead of in the gaseous state as formerly. The solution thus added may contain sulphites, and compounds are more likely to be formed in the wine which are capable of precipitating barium chloride if the wine be much exposed to the air and to acids as in the gravimetric process. In practised hands, the simple volumetric process is most satisfactory. This consists in adding standard barium chloride solution to the boiling wine, filtering a little, and testing to ascertain that no further precipitation follows the addition of either barium chloride or saturated calcium sulphate solution. J. T.

Detection of Fahlberg's "Saccharin" in Articles of Food. By E. Börnstein (*Zeit. anal. Chem.*, **27**, 165—168).—For detecting it in sugar, Herzfeld acidifies slightly with an acid, shakes with ether, distils the ethereal solution, fuses the residue with soda and nitre, and calculates the amount of sulphinide from a determination of the sulphuric acid. Schmitt's method depends on the formation of salicylic acid when the "saccharin" is fused with sodium hydroxide, but the absence of ready formed salicylic acid from the material under examination is an essential condition.

The author relies on the following reaction:—A solution of "saccharin" in strong (25 to 30 per cent.) potash treated with bromine drop by drop until a permanent yellow colour remains, yields on cooling a yellow, pulpy precipitate, which shows transparent, yellow prisms and needles under the microscope. Heated on platinum, it swells in vermicular forms, and leaves a bulky coal containing potash. Heated with water, it evolves bromine and slowly dissolves. The solution on cooling deposits at first yellow, transparent crystals with acute-angled edges; on concentrating the mother-liquor, white satiny plates are obtained. These substances are being further examined. 0·01 gram of "saccharin" is sufficient for recognition in this manner. A more delicate test is based on an observation of Remsen's (*Amer. Chem. J.*, 1887, 372). A minute quantity of "saccharin" heated in a test-tube with a small excess of resorcinol and a few drops of strong sulphuric acid turns yellow, red, and then deep green, and effervesces strongly from escape of sulphur dioxide. After cooling and dilution with water, an excess of alkali is added, when a solution is obtained which appears red by transmitted light, but with a strong green fluorescence. A milligram of saccharin is enough to give 6 litres of fluorescent solution. To examine an article of food by this means, the substance is exhausted with ether after slightly acidifying, best with phosphoric acid. Chocolate should first be freed from fat by light petroleum, then mixed with phosphoric acid and sand, and dried at 100° before extraction with ether. Remsen's observation relates to orthosulphobenzoic acid, but it appears that commercial "saccharin" consists to a great extent of this substance mixed with parasulphaminebenzoic acid. It is, however, highly probable that the pure sulphinide would also give the fluorescence reaction.

M. J. S.

Action of Oils on Polarised Light. By Péter (*Bull. Soc. Chim.*, **48**, 483—486).—The results of the examination of the effect of several oils on polarised light are given. It is proposed to determine qualitatively the nature of oils by their action on polarised light, and to this end the author is engaged in making an analytical table. The results yielded by the polariscope, and by a determination of density, and of the heat developed when the oil is mixed with sulphuric acid, are more trustworthy than colour reactions, and are more readily obtained (compare also Bishop, this vol., p. 388).

N. H. M.

Apparatus for the Extraction of Fat in the Cold. By O. Foerster (*Zeit. anal. Chem.*, **27**, 173—175).—The substance is placed in a filter-tube terminating below in a glass worm, the whole being surrounded with a glass water-jacket, and ground into the neck of a flask. A side-tube conveys the vapour from the flask to a second worm above the substance, where it is condensed and cooled before it falls upon the material. Figures of the apparatus (which is made by Müller, of Bonn) are given. M. J. S.

Test for Acetanilide. By F. Flückiger (*Chem. Centr.*, 1888, 26; from *Apoth. Zeit.*, 1887, 410).—If two parts of acetanilide moistened with chloroform is rubbed up with one part of potash, transferred to a flask and gently heated, phenyl isocyanide is formed, which can be readily detected by its peculiar and unmistakable odour. The heat must not be allowed to rise too high, for at 167° phenyl isocyanide boils with decomposition, and at 200—220° it is converted into its isomeride, benzonitrile, which under these circumstances would be converted into a benzoate and ammonia. J. P. L.

Separation of Resins. By G. Kliebhau (*Chem. Centr.*, 1888, 87, from *Pharm. Zeit. Russ.*, **26**, 777—779).—The relative solubility in various solvents, and the behaviour towards acetic, sulphuric, and nitric acids, boiling aqueous soda, and ammonia, afford the best means of separating the different resins. In the following experiments, the powdered resins were treated with three times their volume of the solvent at a temperature of 29—30°. In boiling water, colophony forms a half-melted mass; shellac, mastic, elemi, and dammar agglomerate; sandarach, copal, and amber remain unchanged. In alcohol, mastic, shellac, sandarach, and colophony are soluble; elemi soluble with difficulty; dammar and amber insoluble; copal agglomerates. In ether, dammar, colophony, mastic, elemi, and sandarach are readily soluble; amber and shellac insoluble; copal swells up. Carbon bisulphide dissolves dammar and colophony readily; mastic, elemi, and sandarach with difficulty; amber and shellac not at all, Benzene dissolves dammar, mastic, and colophony; sandarach and elemi with difficulty; whilst amber, shellac, and copal are insoluble. Light petroleum dissolves dammar and mastic readily; colophony, elemi, and sandarach with difficulty; amber, copal, and shellac not at all. Acetic acid causes colophony to swell, but is without action on the other resins. Sulphuric acid dissolves all resins, but causes charring and decomposition; dammar, on the other hand, when treated with sulphuric acid, becomes bright red. Nitric acid colours mastic and sandarach bright yellow; elemi, a dirty yellow. Aqueous soda dissolves shellac readily; colophony with difficulty, but is without solvent action on the others. Colophony dissolves readily in strong ammonia; mastic, sandarach, and copal swell up before dissolving; whilst amber, dammar, shellac, and elemi remain unchanged. J. P. L.

Valuation of Indigoes. By C. Rawson (*Chem. News*, **57**, 7—8, 19—20, 29—30, 34—36).—As much diversity of opinion exists in connection with the valuation of indigoes, the author has investigated the subject and examined the various methods employed. The sample for analysis should consist of small pieces from each lump in the lot sent for analysis, finely ground, and all passed through a sieve. 1 gram of the finely-powdered indigo is mixed with an equal weight of ground glass and gradually added with stirring to 20 c.c. of sulphuric acid (sp. gr. 1·845), it is now placed for one hour in a steam-bath at 90°. The indigotin is then completely dissolved, and the sulphindigotic acid formed is diluted to 1 litre. Of all the methods of estimating indigotin depending on oxidation, the author prefers the permanganate method; a mere titration, however, only gives an approximate estimate, inasmuch as the impurities soluble in dilute acids are also attacked, and so the results are high; the following method is recommended to eliminate this error:—50 c.c. of the filtered sulphindigotic acid is mixed with 50 c.c. of water and 32 grams of sodium chloride; sodium sulphindigotate being almost insoluble in strong salt solution separates, and after two hours is collected, washed with salt solution (sp. gr. 1·2), dissolved in hot water, and when cool acidified with 1 c.c. of sulphuric acid, then diluted to 300 c.c., and titrated with permanganate; a small correction has to be made for the sulphindigotate retained by the salt solution; the results agree very closely with the combined percentages of indigotin and indigo-red.

The hyposulphite method (Abstr., 1881, 310) is fully described and studied; the author finds that neither indigo-gluten, indigo-brown, nor indigo-red have any appreciable effect on the results obtained by this method. Ferric salts, however, cause high results, and in fact a method is suggested for estimating ferric iron by means of hyposulphite.

The sublimation method (Lee, Abstr., 1884, 1438) is inaccurate, inasmuch as pure indigotin suffers decomposition under this treatment, whilst in ordinary indigo many of the impurities are affected, and, therefore, in the first instance the results are too low, and in the second too high.

Methods based on the reduction of indigo in alkaline solutions are not as accurate as is generally supposed; a modified, and apparently tedious, ferrous sulphate and sodium hydroxide method (Crace-Calvert's method) is described in detail, but the following is recommended as most trustworthy:—A gram of finely-powdered indigo is made into a paste with water and placed in a flask with 500 to 600 c.c. of lime-water, the flask is closed with an india-rubber stopper bored with four holes, one carrying a syphon, another a tap-funnel, the remaining two serve for the ingress and egress of a current of coal-gas, the whole is heated at 80°; 100 to 150 c.c. of sodium hyposulphite (Na_2SO_2, not thiosulphate) solution (5 times as strong as the solution used in the acid method) introduced and kept near the boiling point for half an hour, allowed to settle, and 500 c.c. of the clear liquid syphoned off, oxidised by aspirating air through it for 20 minutes, an excess of hydrochloric acid added, and the precipitate of indigotin and indigo-red washed and weighed. The liquid remaining in the flask is measured, and the results calculated on the whole quantity. If the proportion of indigo-red is required, the filter and precipitate are extracted with alcohol in an extraction apparatus, when the red passes into solution. D. A. L.

Allen's Method for the Detection of Hop-substitutes in Beer. By J. O. ARNOLD (*Chem. News*, **57**, 33).—In reference to Allen's method (Abstr., 1887, 1146), the author has not succeeded in removing completely the bitter principle of the hop from beer by precipitation with either basic or normal lead acetate. D. A. L.

Precipitation of Hop-bitter by Lead Acetate. By A. H. ALLEN (*Chem. News*, **57**, 53—54).—A rejoinder to Arnold (see preceding Abstract). The author disclaims the discovery of the process in question, and acknowledges that lead acetate cannot be relied on for the complete precipitation of hop-bitter. He has noticed that solutions which were bitter when the excess of lead was removed from the solution by means of hydrogen sulphide, lost all bitterness when sulphuric acid was employed instead of hydrogen sulphide.

D. A. L.

Precipitation of Hop-bitter by Lead Acetate. By A. H. ALLEN (*Analyst*, **13**, 43).—Contrary to his former experience, the author now finds that lead acetate cannot be relied on for the complete removal of the bitter principle from an infusion of hops. In most cases it succeeds fairly well, but in other cases the residue from the filtrate has a strongly marked bitter taste. By using excess of sulphuric acid instead of hydrogen sulphide for the removal of the lead, the traces of hop bitter left in the filtrate are got rid of during the evaporation. Foreign bitters can, however (according to Adams), always be detected, with the exception of camomile, the bitter of which is precipitated by lead acetate. M. J. S.

Precipitation of Hop-bitter by Lead Acetate. By W. JOHNSTONE (*Analyst*, **13**, 6—7).—The author, having examined a sample of hops of undoubted purity, found that the filtrate from the lead precipitate left a bitter residue. No details are given (comp. Allen, Abstr., 1887, 1146). M. J. S.

Detection of Proteïds in Urine. By S. H. C. MARTIN (*Brit. Med. Journ.*, **1**, 1888, 842—844).—The tests ordinarily applied for the detection of proteïds in urine in clinical work do not distinguish between the numerous substances included under that name. The object of the present paper is to discuss the more modern methods of the separation and detection of proteïds, as applied when those substances occur in the urine. It is necessary that the proteïd should be first obtained free from the other constituents of the urine. This is done by saturating the fluid with ammonium sulphate; by this means, albumins, globulins, and albumoses are precipitated. The precipitate is collected, washed with saturated solution of ammonium sulphate, and redissolved by the addition of water; the presence of a small amount of ammonium sulphate in this solution does not interfere with their distinctive properties. *Albumins* may be recognised in this solution by the fact that they are not precipitated by saturation with magnesium sulphate, and that they coagulate by heating their solutions to about 73°. Egg albumin is coagulated by ether, serum albumin (the proteïd which most frequently occurs in urine) is not. *Globulins* on the other hand, are precipitated by saturation with magnesium sulphate; serum globulin, which is practically the only globulin that is ever present in urine, coagulates by heat at about 75°. Of *albumoses*, that which most frequently occurs in urine is heteroalbumose. This is precipitated by heat even when no acetic or other free acid is added, whilst albumins and globulins are not; this precipitate comes down at 43—50°, and is soluble in a few drops of weak acid; coagulated albumin or globulin is not. This substance also gives the characteristic nitric acid test for albumoses, and the biuret reaction. It is moreover precipitated by saturation with magnesium sulphate. If other albumoses or globuloses are present, the various distinctive tests as described by Kühne and Chittenden must be applied. The only method for determining the presence of *peptones* in urine is the fact that they are not precipitated by saturation with ammonium sulphate; any proteïd remaining in solution after the precipitation of other proteïds by saturation with that salt must be peptone; it may be identified in such a saturated solution by the xanthoproteic and biuret reactions. W. D. H.

Action of Bleaching Agents on Writing Ink. By R. IRVINE (*J. Soc. Chem. Ind.*, 6, 807—808).—The author made a series of experiments to ascertain whether it is possible to tell the age of writing, and if writing has been executed at one and the same time, and if so, at what time. He selected writing one day, six months, 12 months, 2 years, 6 years, 14 years, and 22 years old, and exposed these writings to the action of a very dilute solution of bleaching powder, sp. gr. 1·001. In six minutes, the newly-written matter had disappeared; in from nine to 12 minutes, the writing of six months ago had disappeared; in 20 minutes, the writing of two years had partly disappeared, whilst in a like time the writing of six years ago was not greatly affected, of 14 years ago very slightly, and of 22 years hardly at all. Hydrogen peroxide acts more slowly but gives more definite results. When writing ink is thus bleached, most of the iron contained therein remains mordanted with the fibres of the paper, consequently writing so tampered with can be restored by the application of gallic or tannic acid. In determining the age of any particular writing, the following precautions should be observed:—(1) The inks must be those known as ordinary writing inks prepared from iron and chromium salts and galls. (2) Writing dried by means of blotting-paper is more easily removed than writing which is allowed to dry on the surface of the paper. (3) The bleaching solution must be exceedingly dilute, otherwise the action is so rapid and powerful, that both old and new writings are removed almost simultaneously. (4) The action must be carefully watched so as not to be too long continued. (5) Very old writing which has become brown by age, although it resists the action of weak solutions of bleaching powder and hydrogen peroxide, will show signs of giving way almost instantly when acted on by dilute nitric, hydrochloric, or oxalic acids. D. B.

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